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## Research on synthesis and action mechanism of polycarboxylate superplasticizer

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**Abstract** The relationship between the structure and performance of polycarboxylate superplasticizer was analyzed. The respective functions of the structure units of the main and branched chains were discussed. The progress of synthesis and molecular structure design and synthesis of polycarboxylate superplasticizer were reviewed according to the difference in the structure unit of the main chain. Results indicated that their performance is related to the structure unit of the main and branched chains, as well as the position and species of functional groups. The polycarboxylate superplasticizer, which had suitable graft and block polymers of polyethylene glycol or polyoxyethylene, and a suitable sulfonic group, had small slump loss besides high water-reducing performance. On the other hand, the hydroxyl group at the end of the chain causes gelation easily. On the basis of the items mentioned above, as well as the source and cost of raw materials, esterification of polyethylene glycol and acrylic acid were first adopted using para-toluene sulfonic acid as catalyst, then polymerized with sodium sulfonate methacrylate. A certain amount of acrylic was added in order to regulate both the polymerization degree of the main chain and the ratio of carboxyl and sulfonic groups in the branched chain. As a result, the high performance superplasticizer has been synthesized (was obtained). The divergence of the cement plasma is about 200 mm when the addition amount of superplasticizer is 0.16%–0.20% of cement weight, and the ratio of the water and cement is 0.29.

**Keywords** polycarboxylate, superplasticizer, molecular structure design, mechanism of action

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### 1 Introduction

Polycarboxylate superplasticizer is a new kind of plasticizer which appeared in the 1980s [1–4]. A polycarboxylate superplasticizer with suitable hydrophilic functional groups was developed successfully by Nippon Shokubai Company in 1986 [5], and was formally put into industrial use in the mid-1990s. The amount of polycarboxylate superplasticizer had surpassed naphthalene products greatly, and about 80% of the amount of plasticizer was produced in 1995 in Japan. More attention has been paid to polycarboxylate superplasticizer in North America and Europe as well.

Polycarboxylate superplasticizer with carboxyl is a kind of macromolecular surfactant and its molecule looks like a comb, with the active-monomer having carboxyl as the main chain, and the graft copolymer, which is formed from the active-monomer and the functional groups of the main chain, being the branched chain. Because the structure unit of the main and branched chain in polycarboxylate superplasticizer can be changed by using a variety of monomers, its performance is polytropical. On the basis of the polytropy mentioned above, the relationship of the composition, structure, and performance of the plasticizer can be found, and a polycarboxylate superplasticizer molecule with optimal performance can be designed. Therefore, research on polycarboxylate superplasticizer becomes an important issue in the area of gelation material and construction engineering [6–8].

### 2 Synthesis system and action mechanism of polycarboxylate superplasticizer

The molecular structure of polycarboxylate superplasticizer is polytropical, not only varying in the sort of monomer and the position of the functional groups, but also in the molecular weight and molecular weight distribution. According to the different structural units of the macromonomer to be designed in the main chain (mol ratio more than 50%), polycarboxylate superplasticizer may be classified into polyacrylate, poly(maleic anhydride), etc.

## 2.1 Polyacrylate plasticizer

Polycarboxylates were first synthesized by polymerization of pure acrylic acid [9], but the beginning Zeta potential was high and unstable, and the slump constant was controlled. Later, the polycarboxylate was copolymerized by olefin and unsaturated carboxylic acid, but the improved technological conditions were difficult to control, the molecular weight of products was lower and effects were not good as it was applied singly. In order to overcome the problem, researchers tried to change the monomers' polymerization. After a great deal of research, we found that by taking polyoxyethylene as the main chain or introducing polyoxyethylene into the branched chain, the Zeta potential of the products became stable and the slump constant loss could be controlled, and at the same time, the foam could be eliminated [10–12]. Shonaka [11] prepared a series of polycarboxylate superplasticizers that had different degrees of main chains and branched chains, and found that the performance of superplasticizers with a short carboxylate main chain and a long polyoxyethylene branched chain was better than similar polymers with longer main chains and shorter branched chains. In the meantime, Yamashita et al. [13] pointed out that the hydroxyl group at the end of the chain might cause gelation easily, so it was difficult to use in industries. A lot of chain transfer agents, such as mercaptoethanol or isopropanol, etc., needed to be added to abstract the more active atoms from the monomer, such as H and Cl, etc. The idea of chain transfer is to reduce the degree of polymerization and prevent the gelation. The free chain transfer agent, which exists in the product, would influence the effect of the plasticizers. Therefore, Yamashita et al. [13] copolymerized different polyethoxylate unsaturated esters and salts having no hydroxyl group at the end with acrylic unsaturated monomer, and added a suitable third monomer to improve the performance of the plasticizers. In light of the important effects of the sulfonic group in the monomer structure of naphthalene and xylan superplasticizer, Yamashita et al. [13] introduced aliphatic sulfonic anion into the molecule (molecular), which was used as a chain transfer agent. Yamada had researched the influence of the length of chains, the degree of polymerization of the main chain, and the molar percent of carboxy and sulfonic groups in the branched chain of polyoxyethylene polycarboxylate superplasticizers on the dispersion of cement. It was found that the longer the branched chain, the lower the degree of polymerization, the more sulfonic groups, the better the dispersion of plasticizer for the cement.

## 2.2 Poly(maleic anhydride) plasticizer and copolymerized plasticizer

The poly (maleic anhydride) plasticizer was synthesized by using polyethylene glycol (or the block-copolymerization of ethylene glycol and propanediol) as raw materials, esterified first and polymerized subsequently. Alkane hydrophobic groups in the molecules can eliminate the foam and increases the liquidity when it was used as addition agent [16]. In 1995, Matsunaga et al. [17] synthesized the poly(maleic anhydride)

superplasticizers by copolymerization of maleic anhydride, hydroxy-amino-acid and methoxy triethylene glycol. The good effects of dispersion were proven by experiment. At the same time, Honda et al. [18] developed the polycarboxylate superplasticizer synthesized by polyoxyethylene and maleic anhydride (or its derivatives) with addition of diolefin polyethylene oxide, etc. The results indicated that the effects of superplasticizer addition on the copolymerization of the mixture and maleic anhydride were better.

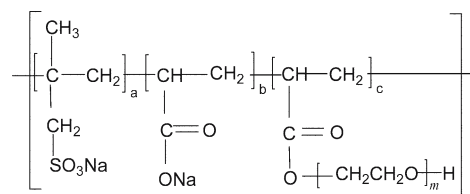
In order to get a superplasticizer with perfect performance, Akimoto synthesized the plasticizers by copolymerization of polychloroethylene and maleic anhydride or (its derivatives). The main chain was oxyalkyl, the branched chain was carboxylic acid. However, the hydroxyl group of the long branched chain caused gelation easily. Hirata then synthesized polycarboxylate superplasticizer using maleic acid as the end group of the polyoxyalkyl branched chain to resolve the gelation problem. Different polymaleic anhydride plasticizers containing appropriate amounts of unsaturated monomer with a sulfonic group on it had a small slump loss besides having a high water-reducing performance. For example, Takahashi synthesized polycarboxylate superplasticizer by copolymerization of a polyoxyalkyl derivative, unsaturated carboxylic acid, and the monomer with  $-\text{SO}_3\text{H}$  on it. The cements containing the superplasticizers mentioned exhibited good characteristics such as high water-reducing property, low viscosity, 25% water removal, and long-lasting strength.

In order to optimize the important action of acrylic acid and maleic anhydride in the main chain, Lim et al. [19] synthesized a block polycarboxylate superplasticizer by copolymerization of maleic anhydride and acrylic acid, then coordinated with the National Science Foundation (NSF). The performance of the plasticizer in terms of adsorbability and liquidity became better. Ohta et al. [20] then found that if sulfonic sodium was introduced into the main chain, the copolymerization of acrylic acid, acrylate and maleic anhydride and the performance of the plasticizer became better.

## 3 Synthesis and characterization of polycarboxylate superplasticizer

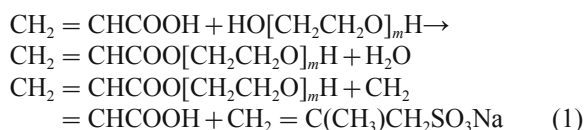
The development of polycarboxylate superplasticizer in our country occurred later, and most of the researches are in.

The authors designed polycarboxylate superplasticizers on the basis of the research on their monomer structure. Acrylic acid was taken as the main chain unit and the ratio of the suitability of the ester was increased. The sulfonic group, polyethylene glycol, was introduced into the main chain, and the molecular structure of the plasticizer with multi-branched chains can be represented as follows



It was found that the synthesized plasticizers not only have high water-reducing performance but also have small slump loss.

On the basis of the results mentioned above, polycarboxylate superplasticizer was synthesized via a two-step process using polyethylene glycol, sodium sulfonate methacrylate and acrylic acid as raw materials. First, the esterification of polyethylene glycol and acrylic acid was carried out to get an esterified macromonomer. Then, the macromonomer, sodium methyl propylene sulfonate, and acrylic acid were copolymerized. The main reactions in the process can be shown below



The optimum reaction conditions can be summarized as follows: the ratio of alcohol and acid was 1:2, the reaction temperature was 100°C–200°C. According to the analysis of the IR spectrum (Fig. 1) and UV spectrum (Fig. 2), the polymer contained a hydroxyl group, a sulfonic group, a carboxylic group, and an ester group, so it was believed that the polycarboxylate superplasticizer has been synthesized by copolymerization of unsaturated monomers containing a hydroxyl group, a sulfonic group, a carboxylic group, and at the same time, the esterification graft chain was an effective way to introduce a long branched chain. According to Gel Permeation Chromatography, the average molecular weight of the plasticizer synthesized is about 3 000 g/mol, which reaches the level of middle molecular weight. When the weight of the plasticizer was 0.17%–0.19% of the cement, the cement paste fluidity was 200 mm (refer to FDN-1), the ratio of water-reduction was more than 28% (water: ash 0.29, cement P.O.42.5, which was the product of huangshi huaxing), the slump constant loss was small, there was little loss within 90 min, and the 28 d compressive strength of the cement paste attained 120%–130%. Therefore, the early strength of cement paste mixed with polycarboxylate superplasticizer had been improved greatly.

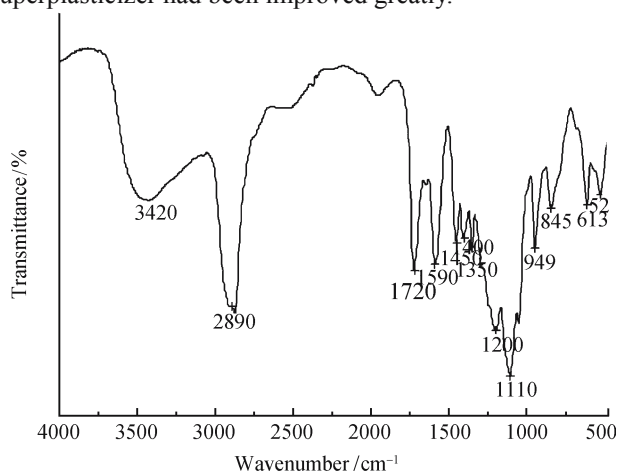


Fig. 1 Infrared spectroscopy (IR) of plasticizer

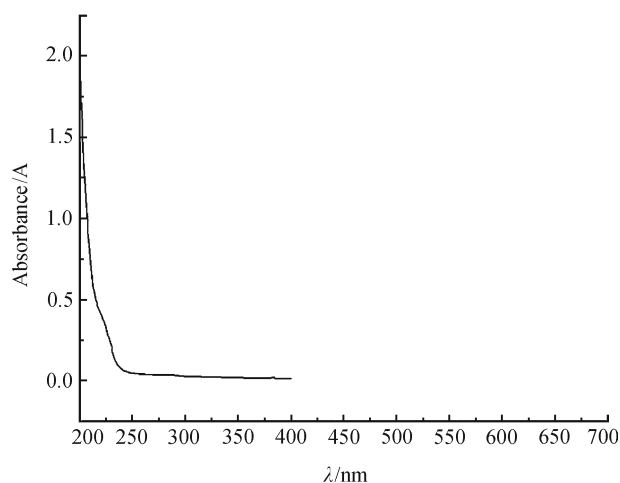


Fig. 2 Ultraviolet (UV) of polycarboxylate plasticizer

## 4 Conclusions

The structural unit of the main and branched chains, the position and effects of the functional groups of the polycarboxylate superplasticizer were discussed. Based on this, the different functional groups were introduced into the main chain to meet industrial application. The superplasticizer comprising strong polar functional groups such as carboxy (–COOH), sulfonic (–SO<sub>3</sub>H), hydroxyl groups in the main chain, as well as increasing the length of the nonpolar group, which connects to the strong polar functional group, can increase the thickness of the solvent, augment electrostatic repulsion and block repulsion of solvation, and therefore improve the dispersity of the products. On the basis of the results mentioned above, a polycarboxylate superplasticizer was synthesized by a two-step method with polyethylene glycol, acrylic acid, and sodium methyl propylene sulfonate as raw materials. When 0.16%–0.20% plasticizer was added into the cement paste, the initial slump constant loss of the cement attained about 200 mm, with no segregation and weepage, and the early strength improved greatly.

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## References

1. Cho H Y, Suh J M. Effects of the synthetic conditions of poly{carboxylate-g-(ethylene glycol) methyl ether} on the dispersibility in cement paste. *Cement and Concrete Research*, 2005, 35(5): 891–899
2. Bradley G, Howarth I M. Water soluble polymers: The relationship between structure, dispersing action, and rate of cement hydration. *Cement Concrete Aggregate*, 1986, (8): 996–1001
3. Lim G G, Hong S S, Kim D S, Lee B J, Rho J S. Slump loss control cement paste by adding polycarboxylic type slump-releasing dispersant. *Cement and Concrete Research*, 1999, (29): 223–2291

4. Spiratos N, Jolicoeur C. Trends in concrete chemical Admixtures for the 21st century. In: the Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete. Nice: France, 2000, 10: 1–15
5. Hirata T, Yuasa T, Shiote K, Iwai S, Nagare K, Tahara H. Method for dispersion of cement, USP6048916, 2000–4–11
6. Etsuo Sakai, Akira Kawakami, Masaki Daimon. Dispersion mechanisms of comb-type superplasticizers containing grafted poly (ethylene oxide) chains. *Macromol Symp*, 2001, 175(3): 367–376
7. Li C Z, Feng N Q, Wang D M. Preparation and characterization of comb-like polycarboxylic water-reducers and its function mechanism. *Journal of the Chinese Ceramic Society*, 2005, 33(01): 87–92
8. Kazuo Yamada, Tomoo Takahashi, Shunsuke Hanehara. Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer. *Cement and Concrete Research*, 2000, 30(2): 197–207
9. WANG G J, Huang H Y. Synthesis and Characterization of Polycarboxylate High Range Water-reducer. *Chemical Materials for Construction*, 2003, (06): 47–51 (in Japanese)
10. Li C Z, Feng N Q, Li Y D. Effects of polyethylene oxide chains on the performance of polycarboxylate-type water-reducers. *Cement and Concrete Research*, 2005, 35(5): 867–873
11. Shonaka M. Polymer technology reshapes water reducers. *Concrete Products*, 1998, (10): 5
12. Yamashita A, Tanaka H, Yamamoto M, Uno T, Onda Y, Hirata T. Cement dispersant and cement composition comprising this. USP6569234, 2003–5–27
13. Yamashita A, Hirata T, Yuasa T. Cement admixture and cement composition. USP6294015, 2001–9–25
14. Uchikawa H, Hanehara S, Sawaki D. The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture. *Cem Concr Res*, 1997, 27(1): 37–50
15. Ota A, Sugiyama Y, Tanaka Y. Fluidizing mechanism and application of polycarboxylated-based superplasticizers. In: *The Fifth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*. Rome., SP173, 1997, 359–378
16. Yoshioka K, Sakai E, Daimon M, Kitahara A. Role of Steric hindrance in the performance of water-reducers for concrete. *Journal of the American Ceramic Society*, 1997, 80(10): 2667–2672
17. Matsunaga T, Takei K, Toba T, Ikeuchi H, Tamura F. U S process for producing polymer having hydroxyl groups at both terminals. USP5391665, 1995–02–21
18. Honda S, Hara T, Koyata H. Dispersant composition for cement having excellent property in inhibition of slump-loss. USP5432212, 1995–07–11
19. Lim G G, Hong S S, Kim D S, Lee B J, Rho J S. Slump loss control of cement paste by adding polycarboxylic type slump-releasing dispersant. *Cement and Concrete Research*, 1999, 29: 223–229
20. Ohta S, Tomomi T Y. Cement dispersing agent. USP5660626, 1997–08–26