

## Review Article

# Progresses in Synthesis of Polycarboxylate Superplasticizer

Shuncheng Xiang <sup>1</sup>, Yingli Gao <sup>1</sup> and Caijun Shi<sup>2</sup>

<sup>1</sup>Key Laboratory of Special Environment Road Engineering of Hunan Province, Changsha University of Science & Technology, Changsha 410114, Hunan, China

<sup>2</sup>College of Civil Engineering, Hunan University, Changsha 410082, China

Correspondence should be addressed to Yingli Gao; [yingligao@126.com](mailto:yingligao@126.com)

Received 8 April 2020; Revised 8 May 2020; Accepted 29 May 2020; Published 3 July 2020

Academic Editor: Fan Gu

Copyright © 2020 Shuncheng Xiang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The prerequisite to synthesize PCE was to prepare new macromonomers with controlled molecular mass, adjustable hydrophilic-lipophilic groups, long-chain alkyl groups, and large terminal hydroxyl groups as well. Structural modifications in the molecular scale of polycarboxylate superplasticizer (PCE) would lead to changes in properties of dispersion and water retention as well as enhancement in the compatibility of Portland cement and so on. This paper reviewed recent developments from synthetic methods of macromonomers as the initial step of production of PCE, PCE at room and elevated temperatures, and relationships between structure and properties of PCE. Through the analysis of references, it was found that PCE synthesized at room temperature had the same performance with PCE synthesized at elevated temperature in terms of conversion rate and initial dispersion in cement but broader molecular weight distribution. Conclusively, the dispersion of PCE in cement might be explained by multiple theories rather than a single one based on development trends as discussed in this paper.

## 1. Introduction

Polycarboxylate superplasticizer (PCE) was synthesized by unsaturated monomers of carboxylic acid, alkane macromonomers of long chains, and others. It was an excellent cement dispersant which would make great performance in concrete [1]. According to the connection form of its main chains and side chains, PCE could generally be divided into two kinds, polyester and polyether. Structural characteristics of polyester based-PCE were ester bond of its main and side chains [2]. The key of synthetic technique was macromonomer, using methoxy polyethylene glycol and acrylate to make esterification or transesterification. However, there were still some difficulties in this process such as difficulties in polymerization of esterification or transesterification, self-polymerization of small monomers, and many side effects in products [3]. Meanwhile, the reaction of polyether was obtained by radical polymerization, using macromonomers of alkenyl polyglycol ether (carboxylic acids and sulfonic acids) and other small monomers to polymerize in aqueous solution directly [4, 5]. Active groups can react with the  $-\text{COOH}$

group on main chains of polycarboxylate and side chains with the  $-\text{C}=\text{C}-$  double bonds can also be attached to the backbone by radical polymerization. In this way, the structure and properties of polycarboxylate can be changed [6].

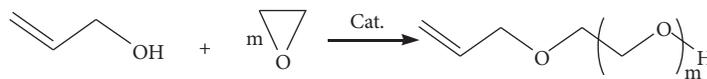
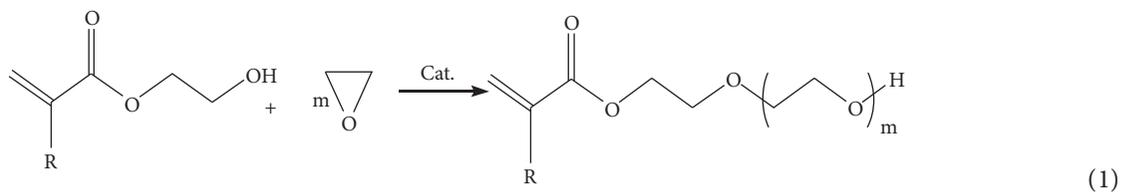
Nowadays, many efforts have been made to improve the structure and the synthesis of PCEs. Plank [7] synthesized polycarboxylates by using acrylic acid and isoprenyloxy polyethylene glycol (IPEG) at  $60^{\circ}\text{C}$  and used  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy to characterize them. The results showed that PCE with optimal dispersing effectiveness was achieved at high contents of IPEG, a molecular weight (Mw) around 40000, and narrow molecular weight distribution. In another study by Liu et al. [8], amide-structural polycarboxylate superplasticizers (amide-PCEs) were produced by amidation reaction between polyacrylic acid (PAA) and amino-terminated methoxy polyethylene glycol (amino-PEG) at  $130\text{--}150^{\circ}\text{C}$ . Yu et al. [9] used butenyl alkylene polyoxyethylene-polyoxypropylene ether (BAPP) as macromonomers and 2, 2-azoisobutyronitrile as an initiator in  $\text{N}_2$  atmosphere for 48 h at  $70^{\circ}\text{C}$ . They tended to

synthesize a polycarboxylate that could greatly accelerate the hydration of cement. In Lange's study [10], acrylic acid and  $\omega$ -methoxy poly (ethylene glycol) methacrylate ester were used to synthesize nonadsorbing polycarboxylates at 80°C within 4 h. It was found that all the synthesized polycarboxylates, which did not adsorb on cement, could enhance dispersion and flowability significantly. Researchers developed excellent PCE with higher water reduction, good adaptability, and other good performances. At the same time, they have been trying to broaden sources of raw materials and synthetic processes, reduce the cost of production, and improve the quality of stability step by step. So, the purpose of this study was to find out their development trends by reviewing the synthesis progress of polycarboxylate, hoping to help the development of this industry.

## 2. Synthesis of Macromonomers

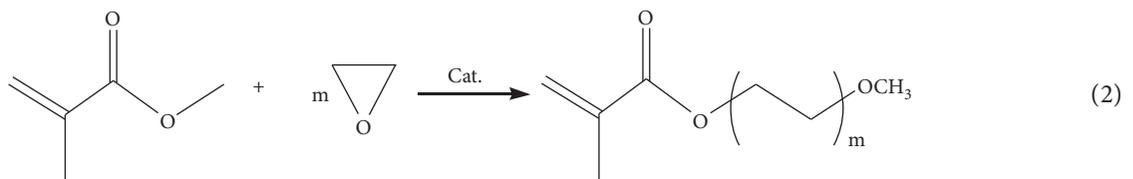
The side chains of molecular structure in PCE were introduced by active other small monomers. Properties such as molecular weight, polarity, and polymerization activity of these active macromonomers were related to the quality and performance of PCE. Methods for their preparation were shown as follows.

**2.1. Ring-Opening Polymerization.** Ring-opening polymerization was used by unsaturated monomers like hydroxyalkyl acrylate or allyl alcohol as initiator which had active hydrogens in terminal chains. Then, by adding oxirane for polymerization, active macromonomers could be obtained. As the principle of the synthesis of polyethylene glycol monomethyl ether, its reaction is shown in the following equation:



By using methyl methacrylate as initiator, about 0.05% amount of metal oxide complex as a catalyst, and some efficient polymerization inhibitor, Poellmann et al. [11] combined propylene oxide and ethylene oxide to ring-opening polymerization and synthesized reactive macromonomers containing both of them, whose reaction temperature was 110°C and pressure was 0.3 MPa. In the autoclave, Kinoshita and Tamaki [12] used allyl alcohol as an initiator and sodium hydroxide as a catalyst at 115°C–125°C, which was added into ethylene oxide for polymerization, and thus, a series of macromonomers with

different molecular weights was synthesized. By polymerizing what he obtained with maleic anhydride, a series of PCE was obtained. In addition, there was a new synthetic method to obtain macromonomers called embedded ring-opening polymerization. By using methyl methacrylate as an initiator and high-temperature melting of Mg-Al hydrotalcite as catalyst, continuous ring-opening reaction mixed with oxirane could be made, which could be embedded into ester bond in methyl methacrylate. A new type of active macromonomer was obtained through the following reaction:

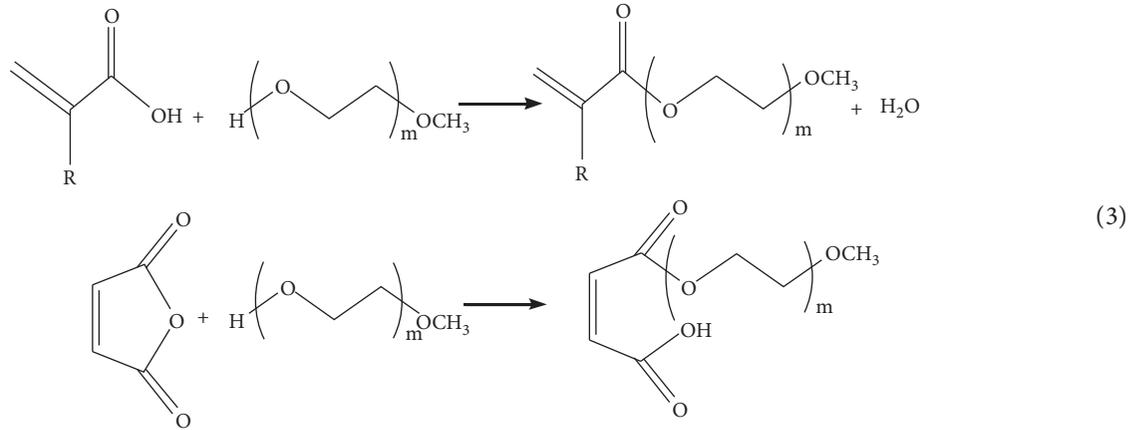


By using phenothiazine as an inhibitor, Keiji and Takafumi [13] calcined Mg-Al hydrotalcite to magnesium aluminum oxide at 500°C and used it into the embedded ring-opening polymerization of methacrylate and ethylene oxide. At 150°C, a new type of

macromonomer was obtained whose molecular weight was several hundred after 5 h. In summary, this method was greatly limited to achieve its industrialization because of its harsh conditions, side effects, low conversion, and slow reaction rate.

**2.2. Direct Esterification.** Direct esterification was used with acrylic acid or maleic anhydride mixed with different molecular weights of polyethylene glycol monomethyl ether to esterify directly and equilibrium conversion

through the reaction in equation (3) as follows. Furthermore, water carrying agent should be used in the process to remove water and make equilibrium shift to the product direction [14]:

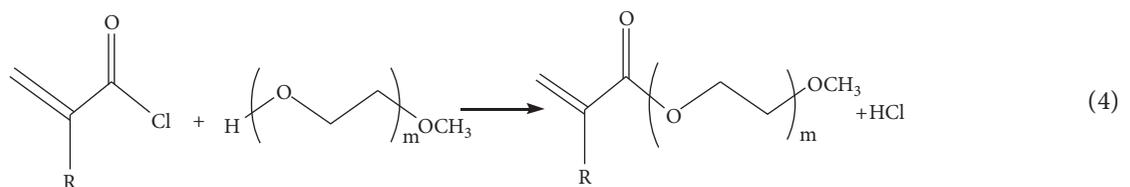


There were some examples. Li et al. [15, 16] used polyethylene glycol to synthesize PCE; meanwhile, methyl allyl sulfonate, acrylamide, methacrylic acid, acrylic acid, and different chain lengths of polyethylene glycol acrylate with polyoxyethylene groups (PEO) were used as small monomers. It was shown in Fourier transform infrared spectroscopy (FTIR) that the molecular structure of modified polycarboxylate superplasticizer (MPCE) contained sulfonic acid groups, carboxylic acid groups, polyethylene oxide vinyl groups, and other groups and had comb-shaped molecular structure. It was also found in gel permeation chromatography (GPC) that the chain length of PEO and the quantity of macromonomers influenced the average molecular weight and its distribution of copolymers of MPCE and thus determined the ability of MPCE to disperse particles of cement. Water reduction would achieve 25% after using MPCE in concrete. In the study of Winnefeld et al. [17], acrylic acid and MPEG were chosen in esterification to prepare macromonomers and the effects of various reaction conditions on the esterification rate were discussed in detail. The optimal conditions were determined as follows: molar ratio of acid to alcohol was 3 : 1, amount of toluene as water carrier was 3%, amount of phenol as inhibitor was 0.8%, and amount of p-toluenesulfonic acid as a catalyst was 1.5%,

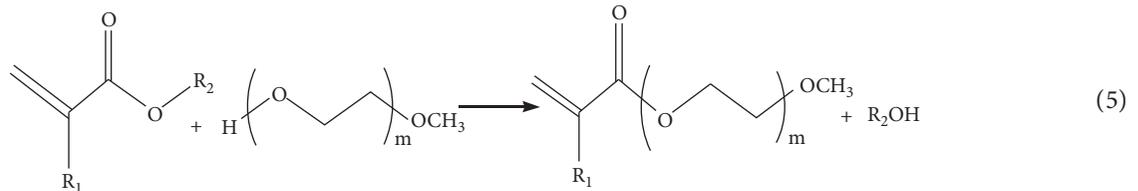
which was esterified for 8 h at 120°C. It could be found in FTIR that macromonomers could be generated under sufficient conditions, which had C=C double bond and methoxy polyethylene glycol acrylate with long chains of polyoxyethylene.

Esterification's rate and extent were affected by many factors, such as temperature, time, the type and amount of catalyst, molecular weight, and MPEG. Thus, the performance of PCE was also affected by those factors [18, 19].

**2.3. Acylation.** Acylation method was begun by methacrylic acid mixed with chloride (like thionyl chloride, phosphorus trichloride, and phosphorus pentachloride). After that, by adding polyethylene glycol monomethyl ether and catalyst, macromonomers of ester or amide could be obtained. Its reaction is shown in equation (4) as follows. It was considered that the method of acylation was an irreversible process with high reactivity. But the drawback was that methacryloyl chloride had poor stability and is easily decomposed and difficult to save for a long time, and its cost was much higher than corresponding carboxylic acid, so there were some limitations applied in the industry:



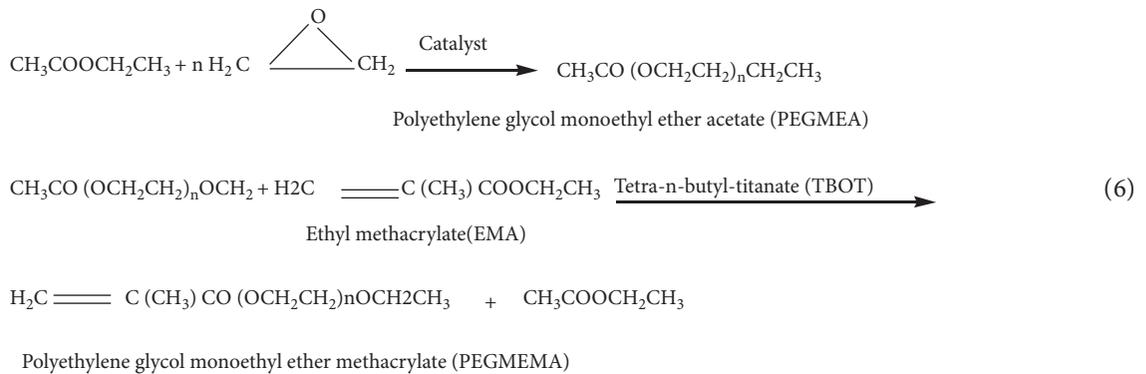
Feng et al. [20] modified MPEG and made its terminal hydroxyl group into the mini ones. Then by using methacryloyl chloride as the acylating agent, MPEG modified in acid chloride reactions was happened and active monomers with double bond were prepared. It was shown in FTIR that the linkage of main chains and side chains in the product was changed into amide-imide linkage instead of traditional ester one. Larger hydrodynamic diameter under the same ionic strength and higher water reduction at the same dosage were also shown in such copolymers.



In the study of Wang [21], glycol monoethyl ether acetate was prepared as intermediate first and mixed with methacrylic acid in transesterification. Then, macromonomers of polyethylene glycol monoethyl ether methacrylate were prepared. The optimal conditions for this reaction were as follows: 7% of

2.4. *Transesterification.* This method was considered to make methyl methacrylate (MMA) and polyethylene glycol monomethyl ether together in the condition of catalyst to obtain macromonomers. In order to enhance the ester exchange rate, methanol alcohol and other small molecules generated in the process should be removed continuously because of its reversibility. Its reaction is shown in the following equation:

tetrabutyl titanate was used as catalyst, 0.1% of 2,2,6,6-tetramethylpiperidine oxide was used as inhibitor, the reaction temperature was 130°C, and the reaction time was 3 h, and the conversion rate of macromonomers could achieve 88.7%. Its reaction is shown in the following equation:



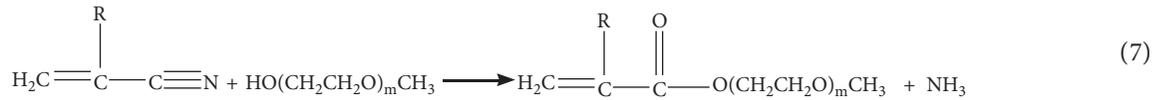
In FTIR, C=O bond of the carboxyl group in 1717 cm<sup>-1</sup>, C-O-C bond in 1107 cm<sup>-1</sup>, and C=C bond in 1636 cm<sup>-1</sup> could be found easily, which illustrated C=C double bond and long polyoxyethylene chains in the product.

In Hao's study of transesterification [22], methyl methacrylate and MPEG were used as raw materials, phenothiazine was used as inhibitor, and sodium hydroxide was used as catalyst. Methanol was removed under reduced pressure at 50°C. The reaction time was 3 h and the conversion rate was 99%. In FTIR, the absorption peak of carboxyl appeared while the absorption peak of hydroxyl disappeared, which indicated a high rate of esterification in the product. Zhang [23] synthesized methoxy poly(ethylene oxide) methacrylate (MPEOMA) macromonomer with

methyl methacrylate and methoxy poly(ethylene oxide) monoether (MPEO,  $n = 23$ ) by transesterification reaction and screening out suitable catalyst, inhibitor, and synthesis conditions. The ideal transesterification rate of about 98% could be obtained.

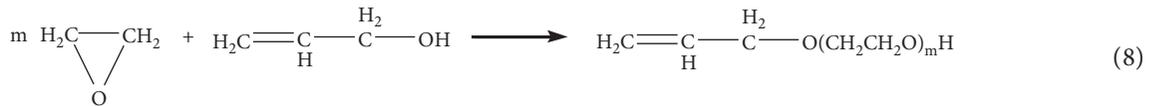
## 2.5. Other Methods

*Direct Aging Method.* In practical applications, methacrylic acid was generally obtained by hydrolyzing corresponding nitrile. So, if hydroxy donor was replaced by alcohols, esters could be obtained directly. Its reaction is shown in the following equation:



Polymerization was done by using alcohol and ethylene oxide. Olefinic alcohol instead of ethylene glycol alcohol could be directly polymerized to form a

double bond-terminated polyethylene glycol with ethylene oxide. Its reaction is shown in the following equation:



### 3. Synthesis of PCE at Elevated Temperatures

Unsaturated carboxylic acid, maleic acid, maleic anhydride, methacrylic acid, alcohols, ethers, hydroquinone, and polyalkenyl hydrocarbons were synthetic materials of PCE. There were some available synthetic methods such as direct polymerization, functional polymerization, graft polymerization, and radical polymerization.

**3.1. Direct Polymerization.** This method was considered to introduce side chains of polyether into the main chains, which needed polymerizable reactive macromonomers like methoxy polyethylene glycol acrylate, and then, a certain ratio of monomers should be mixed together directly in the solution.

Huang [24] chose different monomers, ratio of various monomers, and adjusted reaction process. A series of PCE was synthesized with allyl alcohol polyethylene glycol (APEG, EO=45), acrylic acid (AA), maleic anhydride (MAL), 2-acrylamide-2-methylpropane sulfonic acid (AMPS), and ammonium persulfate (APS) as well. To determine the optimum process of PCE, various reaction conditions for PCE were intensively investigated, such as reactant concentration, temperature, and the molecular ratios of monomers. Sun and Lei [25] synthesized PCE based in aqueous solution polymerization by methyl acrylic acid (MAA), methoxy polyethylene glycol methacrylate (MPEGMA), and sodium methyl acryl sulfonate (SMAS). There were optimum reaction conditions he considered as follows: the ratio of n(MA): n(AA): n(XPEG) was 2:2:1, amount of initiator was 1.5%, the reaction temperature was 70°C, and the reaction time was 6 h.

Ran et al. [26] synthesized two different groups of comb-like copolymer dispersants with side chain lengths ranging from 8 to 48 by direct polymerization. Plank et al. [27] synthesized a new kind of methacrylate polycarboxylate with polyoxyethylene side chain hydroxyl groups at its terminal in side chains, which was different from the traditional one with methoxy side chains. It was shown that there was a comb structure in copolymer which had good adaptability in cement. Also, it had good application prospects. Yamada et al. [28] analyzed the characteristics of PEO's side chain

length and degree of polymerization. It was shown that the effects of chemical structure on the paste fluidity were not significant at high w/c. Zhu et al. [29] synthesized PCE in the water solution by using allyl alcohol polyoxyethylene (APEG), methacrylic acid (MAA), maleic anhydride (MA), and sodium methacrylic sulfonate (MAS) as monomers and the ammonium persulfate as initiator. The optimal synthesis conditions were determined as follows: n(MA): n(MAA): n(APEG): n(MAS) = 215:310:110:0.5, the initiator dosage was 5% of the monomer weight, and the reaction time was 4-5 h. It was considered that a certain proportion of the anionic polar groups (such as -COOH and -SO<sub>3</sub>H) were introduced into main chains in PCE, and thus, hydrophilic main chains were generated, which had strong hydrogen bonds in water. They could form a stable three-dimensional hydrophilic protective layer and provide steric hindrance. By adjusting the proportion of each functional group of polymer's main chains and side chains, structural balance was achieved in order to improve water reduction [30].

Sun and Huang [31] used direct polymerization to make new PCE, which was directly polymerized using allyl polyethylene glycols, methyl acrylate, maleic anhydride, and ammonium persulfate. The influence of monomer ratio, initiator dosage, reaction time, reaction temperature, and dropping time on dispersing ability and fluidity-retaining ability of PCE was studied. Based on the orthogonal experiment, the best process was obtained. The comparison was made on the performance of the product synthesized and another widely used product at present which was synthesized by methoxy polyethylene glycol (MPEG) and methyl acrylic acid (MAA). Lv et al. [32] synthesized a new kind of PCE by introducing citric acid to polycarboxylic molecule as branch in order to solve concrete's slump loss, bleeding, and segregation. Excellent PCE was obtained when n(PEGAA): n(PEGCM): n(MA): n(AA): n(SAS) = 1:0.1:0.3:0.2:0.05, initiator was 0.8% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> by mass of vinyl monomers, the reaction time was 2-3 h, and the reaction temperature was 80°C. It was shown in application result that water-reducing ratio of the product reached 32%, retardation time extended 5 h, and concrete with PCE had excellent slump retention, without segregations and with high compressive strength. Direct

polymerization was completed by a two-step process to obtain PCE, which could obtain excellent products with high purity. However, it was also considered to cost more due to its complexity [31, 32].

**3.2. Functional Polymerization.** Functional polymerization was considered as a kind of modification on the basis of the original polymer. The usual practice was to esterify and graft polyether into main chains at high temperature.

Sun et al. [33] grafted alkoxyamine as a reactant with PCE in the amount of 10–20% of  $-\text{COOH}$  mole. The mixture lasted at  $150^{\circ}\text{C}$  for 1.5–3 h, and then some catalyst was added, the mixture was cooled at  $100\text{--}130^{\circ}\text{C}$ , and the desired product was obtained. Wang and Feng [34] used some proportion of MAS, water, and ammonium persulfate in a three-necked flask equipped with condenser and stirrer and heated them to  $80^{\circ}\text{C}$  to gain yellow liquid after 3.5 h. Then, he mixed polyethylene glycol monomethyl ether and dimethyl sulfoxide in it at  $110^{\circ}\text{C}$  and the reaction mixture was refluxed 5 h, and a new kind of PCE whose solid content was about 30% was obtained. Peaks of  $-\text{OH}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{C}=\text{O}$ , and  $\text{C}-\text{O}$  could be found obviously in FTIR. When the molar ratio of carboxyl, sulfonic acid, and polyoxyethylene in side chains was 0.542 : 0.354 : 0.104, the best performance would be gained in graft copolymer.

Ferrari et al. [35] synthesized a series of PCE depending on the branch length, density, and molecular weight and did some tests of it. The results showed that fractions of higher molar weight were adsorbed to a larger extent than fractions of lower molecular weight. Yang [36] used azobisisobutyramidine hydrochloride (AIBA·2HCl) as initiator in polymerization of polyoxyethylene allyl ether (APEG) and maleic anhydride (MA) to synthesize PCE-1. Also, Isoamyl enol polyoxyethylene ether (TPEG), the activity of acrylic acid (AA) and methacrylic sulfonate (MAS) was used to synthesize PCE-2. The results showed that when mixing PCE with concrete, the slump-retaining ability and the performance of late compressive strength of concrete enhancement were better than the similar PCE which was initiated by ammonium persulfate (APS). Yu [37] used allyl alcohol polyoxyethylene (APEG), acrylic acid (AA), maleic anhydride (MAD), and sodium methyl acrylamide (SMAS) as main raw materials to gain PCE. The compatibility between PCE with cement was excellent. The configuration concrete had excellent characteristics such as lower slump loss. The water-reducing ratio in concrete was 32.4% at the solid dosage of 0.3%.

Du [38] used maleic anhydride, methyl methacrylate sulfonic acid sodium, and allyl base polyethylene glycol (PEG) as raw materials and ammonium persulfate as initiator, and he synthesized poly malay PCE, according to the cement paste slurry flow degree tests to determine the best synthetic process conditions for the poly malay PCE: maleic anhydride, PEG, and methyl methacrylate sulfonic acid sodium with the best molar ratio 4 : 1 : 0.2. PEG with molecular weight of 2400 was selected, the initiator was added in two portions, and the polymerization was carried out at  $80^{\circ}\text{C}$  for 5 hours. Hu [39] researched on the influences of a

single factor in synthesis, confirming the optimal ratio of raw materials, testing the performance of PCE, and characterizing the molecular structure. It was indicated in test results that the expected functional group was introduced into the structure. According to the measured data of GPC, the  $M_w$ ,  $M_n$ , MCL, and SCL of APEG and TPEG type PCE were followed by 14700 g/mol and 103000 g/mol, 7540 g/mol and 84500 g/mol, 2.5 nm and 1.8 nm, and 15.3 nm and 15.3 nm.

Still, there were some problems existing in functional polymerization, for instance, more difficulties to adjust the composition and molecular weight, poor compatibility of PCE and polyether, and difficulties in practical esterification. In addition,  $\text{H}_2\text{O}$  generated constantly would lead to phase separation in esterification. So, it was the key for choosing a suitable polyether with excellent compatibility.

**3.3. Graft Polymerization.** This method was mainly to overcome the drawbacks of functional polymerization where we could control the molecular weight of polymer's main chains, avoiding the poor compatibility issues of PCE and polyether. In polymerization time, side chains could be introduced into main chains by using polyether monomer containing  $-\text{COOH}$  groups. Otherwise, it would be so hard to graft them.

Hamada et al. [40] synthesized a new type of PCE, whose main chains were combined by methyl methacrylate and side chains were esterified by hydroxyl terminated. They obtained branched chains of PCE with good adaptability to cement and strong early performance. Shawl [41] dropped acrylate monomers, chain transfer agent, and initiator in a solution containing methoxy polyethylene glycol at  $60^{\circ}\text{C}$  for 45 min, gradually. Then, he warmed the system to  $120^{\circ}\text{C}$ , removed water under protection of  $\text{N}_2$ , added catalyst at  $165^{\circ}\text{C}$ , and grafted it for 1 h. Finally, he obtained a new kind of PCE with good dispersion, small slump loss, and low-lead gas performance. Cho and Suh [42] made a series of experiments of polymerization and tried to find the relationship between synthetic conditions and the dispersibility in cement paste. The optimum conditions of temperature, initiator (APS), and reaction time were  $70^{\circ}\text{C}$ , 0.5%, and 9 h.

Wang et al. [43] synthesized comb-shaped PCE with methoxy poly methacrylate (MPEOMA), methacrylic acid (MAA), acrylic acid (AA), and sodium allyl sulfonate (SAS) through aqueous copolymerization initiated by ammonium persulfate. It indicated that such PCE has high dispersing ability and good compatibility with various cements. The fluidity of cement paste could attain as high as 265 mm at the dosage of 0.3% and w/c of 0.26. The yield product was more than 96.8%. Zeng [44] synthesized a series of polyether kind of PCE by taking allyl polyethylene glycol (AEO), maleic anhydride, and sodium vinyl sulfonate as monomers of polymerization by aqueous solution free radical polymerization. The study was made on the influence of the synthesis process on the performance of water-reducing agent. The result showed that when the mass ratio of allyl polyethylene glycol (AEO) to maleic anhydride was 3 : 5, dosage of initiating agent was 6–7% of monomer total mass, and the reaction temperature was  $75\text{--}85^{\circ}\text{C}$ .

#### 4. Synthesis of PCE at Room Temperature

Compared to the synthesis of PCE at elevated temperatures, synthesis of PCE at room temperature was direct polymerization of polymerizable monomers [45–47]. Oxidizing agent was added to the system first and some reductive substances were added dropwise, making use of heat and free radicals produced by redox reaction to initiate and maintain whole polymerization [48].

*4.1. Initiator System Using Vc as Reducing Agent.* Due to its strong reduction and special structure, vitamin C was a major reducing agent in the synthesis of PCE [49]. With oxidizing substances, it could produce heat and free radicals easily, so that we could make use of vitamin C to synthesize PCE. Furthermore, this reaction system consisted of vitamin C and hydrogen peroxide [50, 51].

Jiang et al. [52] made a series of experiments to synthesize PCE and reported the best reaction conditions as follows:  $H_2O_2 : Vc = 4 : 1$  (redox initiator system), 1.5% dosage of hydrogen peroxide (mass of macromonomer), 1.2% dosage of sodium phosphate (mass of macromonomer, used as a chain transfer agent), and 6% dosage of SMAS (mass of macromonomer), at room temperature (20–40°C) for 3 h, which could synthesize high-performance PCE with extra high concentration (80%). It was shown in results that paste fluidity could reach up to 285 mm, 60 min net paste fluidity could be 288 mm, and 120 min net paste fluidity could be 282 mm with little loss when 0.20% dosage of PCE was used. Meanwhile, its concrete application performance was good, and water-reducing rate reached 30%. Yang et al. [53] synthesized PCE by using free radical copolymerization of dendritic activated macromonomers and acrylic acid in water. Optimal reaction conditions were using the L-ascorbic acid and hydrogen peroxide as initiators, and dosages of L-ascorbic acid and chain transfer agents were 1% and 2% of monomers. The molar ratio of acrylic acid (AA) and macromonomers was 4:1, AA dropping for 3 h. The concentration of polymerization was 50%. It was shown in GPC that the average molecule weight was 47500, and the conversion ratio of DAM was about 89.6%. The comb-branching PCE showed superior dispersion and slump retention in concrete, compared with the ordinary one. Guan [54] synthesized a new type of PCE with 2-methyl allyl polyoxyethylene ether (HPEG), acrylic acid (AA), and methyl acrylate (MA) as monomers, ammonium persulfate (APS) and vitamin C-hydrogen peroxide ( $Vc-H_2O_2$ ) as complex initiators, and thioglycolic acid (TGA) as chain transfer agent. The best synthesis condition for the radical polymerization was that the mass ratio of raw materials (HPEG:AA) was 8.5:1.0, initiator composed of  $Vc-H_2O_2$  and APS at a ratio of 0.9:1.0 and  $H_2O$  and Vc at a ratio of 5.5:1.0, dosages of MA, total initiator, and TGA were 1.5%, 1.2%, and 0.4% of HPEG mass, and the reaction time was 3 h at room temperature (20°C–40°C). Excellent PCE had a high water-reducing ratio at 33.1% and good slump maintenance and dispersing ability. Guo et al. [55], Wang et al. [56], and Shi also made use of this type of initiating system to

synthesize PCE at room temperature in their patents. There were several advantages of this method such as no need of external heat source, high solid content of PCE, and low cost of products in transportation.

*4.2. Initiator System Using Other Agents as Reducing Agent.* In addition to the initiator system using vitamin C, scientists developed systems using other agents as reducing agent. In addition, other factors such as reducing substance's structure and its electromotive force, the minimum activation energy, and structure of free radicals should be considered seriously [57].

Zheng et al. [58] developed a reaction system consisted of formaldehyde and hydrogen peroxide, adding acrylic acid, maleic anhydride, allyl polyoxyethylene ether, methallyl sulfonate as raw materials, controlling the amount of sulfoxylate total 2.5% of monomer by mass, and the mass ratio of hydrogen peroxide and formaldehyde was 1:1, and thus he obtained PCE with high performance. Wu et al. [59] synthesized PCE under low-temperature condition (15–20°C). It was shown in tests that PCE had similar performance with the one which was synthesized under the high-temperature condition (70°C). This low-temperature synthesis method could reduce steam dosage, save energy, and reduce production cost. Yu et al. [60] used ammonium persulfate as initiator, added dropwise acrylic acid, methacrylic sodium, and chain transfer agent, lasting it for 3 h and adjusting the pH value to five, and obtained a new type of colorless PCE. It could be found in results that PCE synthesized had a certain water-reducing ratio and excellent slump-control capability, 1 h without loss, a suffer less after 2 h. According to the orthogonal experiment, Zhu et al. [61] synthesized PCE by radical polymerization of allyl alcohol polyoxyethylene monomer and other small molecule monomers using redox polymerization with low temperature. The best optimum polymerization conditions were as follows: the molar ratio of monomers  $n(MA) : n(APEG) : n(AM) : n(AA) = 1.6 : 1.5 : 1.5 : 4.0$  and the initiator dosage of sodium dithionite (SD) 4% and  $H_2O_2$  (30%) 4%. The product had a high water-reducing rate and fine slump-retaining ability and could remarkably enhance the strength of concrete.

#### 5. Relationship between Structure and Properties of PCE

Mechanisms of PCE in Portland cement were electrostatic repulsion and steric hindrance due to its hydrophilic and lipophilic groups in chemical structure. Its action form in cement could be divided into eight parts as follows in Figure 1.

Sakai et al. [62] did some experiments and concluded that the longer the chain's length in PCE, the better the dispersion would be, but the fluidity would reduce at the same time. So, short-chain branches were needed to be introduced in it to reduce the flow of losses. In addition, the molecular weight of PCE synthesized was proportional to the square value of initiator's reciprocal concentration, and when the chain

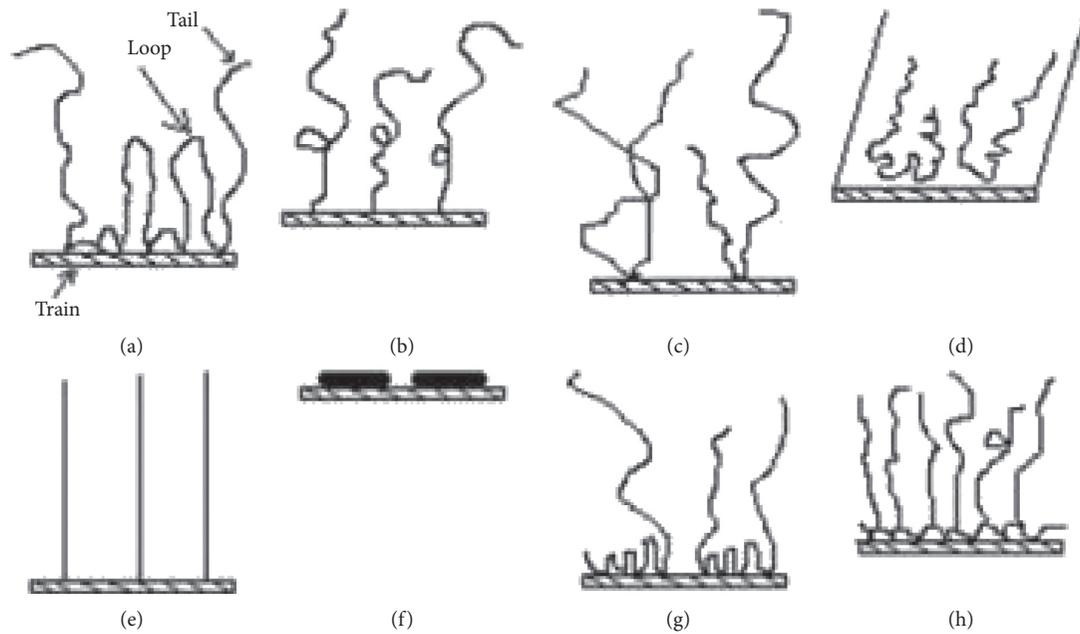


FIGURE 1: Various action forms of PCE (main chains): (a) homopolymer effect (ring-shaped, serial, and caudate), (b) end-effector effect (caudate), (c) role effect (2 caudate), (d) flat-like effect, (e) vertical effect of rigid chain, (f) lying adsorption of rigid chain, (g) effect of block copolymer, and (h) tooth effect of graft copolymer.

length of branched was shorter, the dispersibility would be better. Kinoshita et al. [63] considered that using polyethylene glycol with different chain lengths in the synthesis of PCE could make products achieving high degree of mobility and fluidity. Honda et al. [64] considered that reducing the number of alkyl carbon chain in the synthesis of PCE could lower the air-entraining rate in concrete and the viscosity of copolymer and improve slump. The value of polyoxyalkyl in chain length he preferred was 1–200.

By selecting different side chains of large and small monomers, Plank et al. [65–68] synthesized several kinds of PCE and got rich results of extensive analysis in cement paste. Also, tests of infrared and zeta potential were made and he concluded that electrostatic repulsion and steric hindrance were the key factors. Uchikawa et al. [69, 70] used atomic microscopy and potential instrument to study the mechanism of PCE, and it was considered that steric hindrance in its side chains played a major role in the dispersion of cement instead of electrostatic repulsion which could be ignored. Li et al. [71] synthesized PCE by using MPEGMA, methyl acrylic acid (MAA), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), ethyl acrylate (EA), and acrylamide (AM). The mechanisms of dispersion ability and dispersion retention stability of PCE were investigated using the zeta potential method. The results showed that PCE was advantageous to the strength development of cement and had excellent dispersion retention stability. The dispersibility and dispersion retention stability were correlated with the mole ratio of polymerized monomers, the type of functional groups, and the length of the PEO side chain. The fluidity retention ratio of the cement paste by mini slump spread test with 0.3% (in mass) PCE reached 98.1% in 90 min. Acrylamide (AM), N, N-dimethylacrylamide (DMAA), and 2-acrylamido-2-methylpropane sulfonic acid

(AMPS) were used to replace acrylic acid (AA) in PCE with different proportions. Kong et al. [72] synthesized a series of PCE with different functional groups through radical polymerization. It was shown in the test result that the dispersion performance of synthesized PCE was greatly reduced even was lost if functional monomers of AM, DMAA, or AMPS replaced AA totally. The more the negative charges in the PCE's molecules, the more the molecules of polycarboxylate were adsorbed on the cement pastes. Wang et al. [73] synthesized serials of PCE with the same length of main chains and gradually decreased side chain density via the design of the polymer structure and the optimization of the synthesis technology based on the reaction theory of free radical polymerization. The results showed that the polymerization rate was low when the acid-to-ether ratio was less than 2.5:1 for macromonomers with a polymerization degree of 50. When the side chain density was less than 25%, the initial fluidity of cement paste would not improve obviously. However, the fluid-retaining ability decreased dramatically with the decrease of side chain density.

However, Ran et al. [74] put forward that some kinds of PCE with short side chains instead of long chains also showed good properties of dispersion in cement. Except for steric hindrance and electrostatic repulsion, the lubricating effect of water molecules interact to PCE was also considered as a factor in its dispersion by some scientists [75, 76]. Thus, dispersion of PCE in cement could not be explained by a single theory and we should notice all the ones [77, 78].

**5.1. Effect of Main Chains.** Selecting PCE with suitable molecular weight had an important influence on its performance. The degree of polymerization of PCE, whose

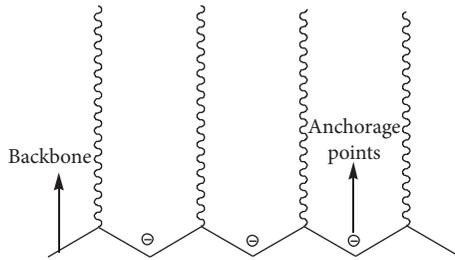


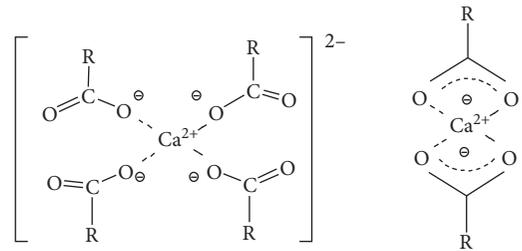
FIGURE 2: Structure of main chains of PCE.

structure of main chains and anchorage points is shown in Figure 2, determined its molecular weight, thereby affecting its adsorption performance [79]. Generally, the higher the molecular weight was, the better the adsorption of PCE would be. However, if the molecular weight was too large, a polymer chain could be attached to several cement particles, and flocculation would occur, which was extremely unfavorable. Some scientists considered that the lower the molecular weight was, the better the property of dispersion would be [80]. But dispersion of PCE would decrease when the molecular weight was too small [81].

Adsorption of PCE could be divided into physical adsorption (iso charge electrostatic adsorption) and chemical adsorption (embedded), while physical adsorption mainly preferred to electrostatic adsorption of carboxylic groups, sulfonic groups, and hydroxyl groups in main chains to salt of calcium silicate or aluminum silicate, and chemical adsorption was the main factor [82]. When PCE embedded layered structure of hydration products of  $C_3A$ , it would no longer contribute to the dispersion, and the dispersion would decrease [83]. Ionized carboxylate anion could control the charge density of ion surface, which could be increased by adjusting pH and ionic strength [84]. Thus, its adsorption would be improved. However, ionization of PCE would be influenced by  $Ca^{2+}$  and  $Na^+$ , bringing about monodentate ligand or bidentate complex as follows in Figure 3, which was negative to its absorption and dispersion [69]. In addition, positive ions also changed the charging characteristics of cement particles, so negative ones and inert components could also get the ability to adsorb PCE [85].

Sulfonic groups could be highly ionized under moderate acidic conditions and adsorbed onto the cement particles with positive charge [86, 87]. In addition, more and more research studies showed that sulfonic acid group was functional to PCE, which could make the dispersion of cement better and lead to high flowability [19, 88].

**5.2. Effect of Side Chains.** When the side chain of PEG of polymerization degree increased from 0 to 130, adsorption of PCE was also gradually decreasing, changing from flat adsorption to vertical adsorption. Thus, best dispersion PCE would occur by using short side chains (less than the degree of polymerization: 34). Winnefeld et al. [17] also conducted some similar studies like Plank. He put forward that the main chains of PCE have no significant effect on improving the workability of cement without side chains. When the chain of PEG was shorter, the relationship between side

FIGURE 3: Complexation of  $Ca^{2+}$  and PCE.

chains' density and workability could be ignored. Only the length of side chains became suitable (the degree of polymerization was 23–45), and liquidity of cement could be improved by low density of side chains of PEG. Chen et al. [89] also studied the influence of PEG to PCE, indicating that water reduction, flexural strength, and compressive strength would be their maximum when the degree of polymerization of PEG was 23. Vickers et al. [90] believed that PCE with high charge density and low grafting would be consumed faster. So, grafting density was also an important factor affecting the performance of PCE.

Except for the length and density of grafting in side chains of PCE, connections and species of side chains would also affect the performance of it. Li [15] studied on the performance of PCE synthesized by different species of connection, concluding that the performance of PCE synthesized by an appropriate proportion of block instead of grafting would be improved. But too much blocks might be negative to the comb structure of PCE. Plank et al. [27] studied difference in the performance of PCE terminated with  $-OH$  and  $-CH_3O$  in side chains, finding there were not too much differences between them due to their similar chemical structures. In other words, they could be replaced by each other.

**5.3. Effect of Molecular Forms.** Form PCE was generally divided into two parts named comb-shaped and hyperbranched. There were more reports about the former for its long history relatively.

Li et al. [91] synthesized a new kind of PCE with comb structure containing polyethylene oxide (PEO) graft chains (PEO side chains). The blended monomers consisted of acrylic acid and polyethylene glycol which was partially esterized with the overdosed acrylic acid. It was shown that the fluidity of cement paste could be reduced a lot by PCE synthesized by an appropriate chain length of PEG. Guo et al. [92] prepared novel amphoteric polycarboxylate (APC) by solution copolymerization and considered that steric repulsion between the cement particles covered by polymer molecules made cement have better dispersion.

By using maleic anhydride, diisopropanolamine, and diethanolamine as main raw materials, Amin et al. [93] synthesized hyperbranched PCE and achieved good water-reducing effect, whose chemical structure is shown in Figure 4. SEM photos showed that the morphology and microstructure of the formed hydrates were affected by the incorporation of PCE.

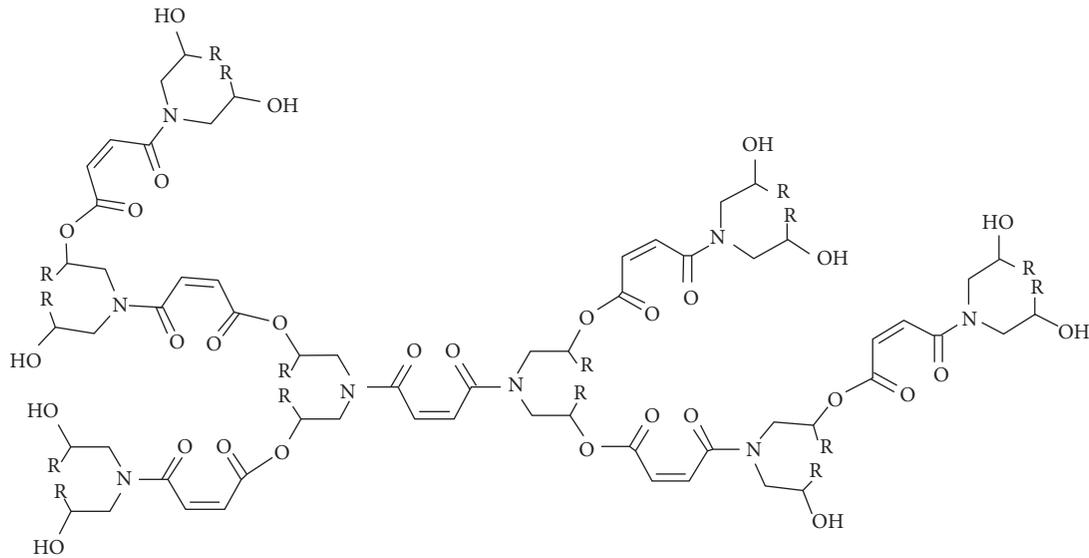


FIGURE 4: Molecular structure of hyperbranched PCE (alcohol amine type).

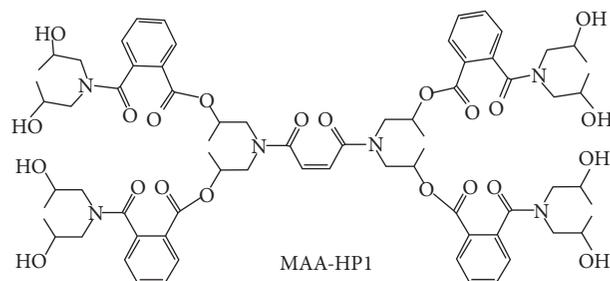


FIGURE 5: Molecular structure of hyperbranched PCE (terminal hydroxyl type).

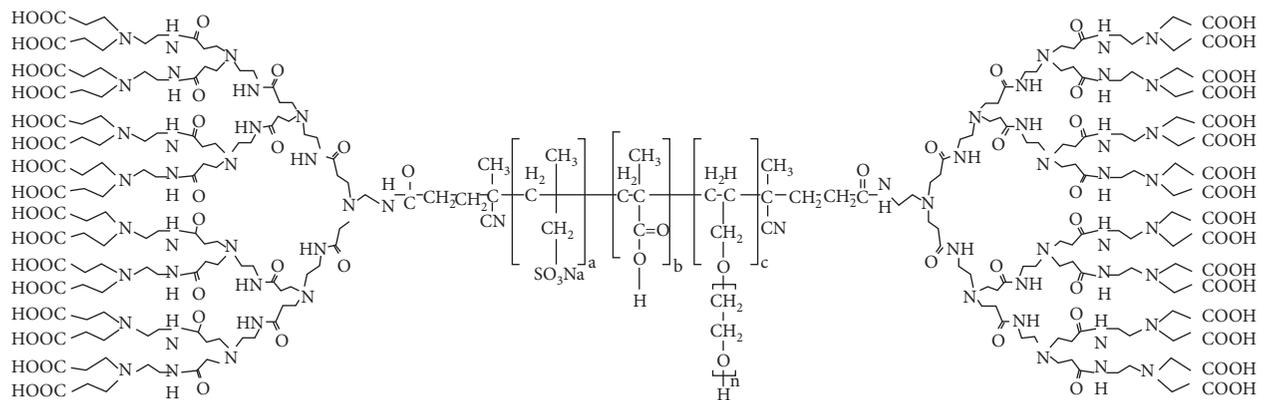


FIGURE 6: Molecular structure of hyperbranched PCE (amide type).

From the perspective of molecular design, Zhi et al. [94] composed a kind of hyperbranched monomer to participate in the main chains of PCE with maleic anhydride, phthalic anhydride, and diisopropanolamine, whose chemical structure is shown in Figure 5. It was shown in results that the polycarboxylate had better cement dispersing performance. The dosage of the chain transfer agent was 1.1%, the

dosage of the initiator was 2.8%, the reaction time was 6 h, and the reaction temperature was 90°C.

Shou et al. [95] synthesized a novel hyperbranched star polycarboxylate superplasticizer (HPC) by ATRP whose chemical structure is shown in Figure 6. It was shown that the novel hyperbranched PCE could be significantly adsorbed on the surface of cement particles.

Obviously, compared with conventional PCE, hyperbranched PCE had more side chains, three-dimensional structures, and better performance on its plastic viscosity, absorption, and flowability.

## 6. Conclusions and Prospects

Through the analysis of references, recent developments from synthetic methods of macromonomers as the initial step of production of PCE, PCE at room and elevated temperatures, and relationships between structure and properties of PCE were reviewed, and the following conclusions could be drawn:

- (1) In order to make PCE's molecular weight controlled and proportion of hydrophilic-lipophilic groups adjustable, macromonomers with reasonable structure and stable performance should be prepared and measures of block and graft to modify existing polyethers and polyesters should be taken.
- (2) Compared with the synthetic products at elevated temperature, PCE synthesized at room temperature had the same performance on conversion rate and its initial dispersion in cement and broader molecular weight distribution, but PCE synthesized at elevated temperature had better performance on collapse resistance.
- (3) Higher content of carboxyl groups of main chains and suitable length of side chains in PCE were so helpful to reduce saturated dosage and improve the performance of it. Dispersion of PCE in cement could not be explained by a single theory and we should notice more factors such as electrostatic repulsion, steric hindrance, chain length of main or side chains, and molecular forms.

Based on the needs of synthesis and application of PCE in cement, there were some prospects of its synthesis and development as follows.

**6.1. Synthesis of Macromonomers and PCE.** Different macromonomers should be explored to synthesize new kinds of PCE in order to enrich its sources. Making use of two or more synthetic methods together might produce better PCE. Every synthetic method above had advantages and disadvantages, superposition of synthesis of PCE could learn from others' strong points and close the gap, and thus the performance of products would be better. For instance, some scholars made use of atom transfer radical polymerization (ATRP) in bulk solution to synthesize PCE, which was considered to be a superposition of direct and radical copolymerization. Moreover, some functional groups might be introduced into main or side chains by blocking or grafting to enrich its performance, such as inhibitor groups, reduction groups, and bubble regulating groups.

**6.2. High Performance.** High performances such as low viscosity, high dispersion, and collapse resistance would continue to be the developments of PCE. In this regard, a new kind of

PCE with hyperbranched structure could better control the rheological properties of fresh concrete, which also had better adaptability and low viscosity. In addition, introduction of zwitterion in PCE was also considered to be a good choice to reduce saturated dosage and achieve its high dispersion.

**6.3. Multifunction.** By designing special structures of molecular, we also could synthesize PCE with special functions such as early strength, antireduction ability, anticracking ability, and antirust ability, which was a trend of development of PCE as well.

## Data Availability

All the data used during the study are available from the corresponding author by request.

## Conflicts of Interest

The authors declare that they do not have any commercial or associative interest that represents conflicts of interest in connection with this work submitted.

## Authors' Contributions

Shuncheng Xiang conceptualized the study, was responsible for methodology, investigated the data, performed data curation and formal analysis, and wrote the original draft. Yingli Gao was involved in project administration, funding acquisition, and supervision. Caijun Shi revised the manuscript.

## Acknowledgments

This project was supported by the National Key R&D Program of China (Grant number: 2018YFB1600100) and Open Fund (Grant number: kfj190503) of Key Laboratory of Special Environment Road Engineering of Hunan Province (Changsha University of Science and Technology).

## References

- [1] C. W. Miao, "High performance admixture for concrete," *Chemical Industry Press*, vol. 4, no. 5, pp. 1-14, 2009, in Chinese.
- [2] B. He, Y. Gao, L. Qu, K. Duan, W. Zhou, and G. Pei, "Characteristics analysis of self-luminescent cement-based composite materials with self-cleaning effect," *Journal of Cleaner Production*, vol. 225, pp. 1169-1183, 2019.
- [3] Y. Gao, L. Qu, B. He, K. Dai, Z. Fang, and R. Zhu, "Study on effectiveness of anti-icing and deicing performance of superhydrophobic asphalt concrete," *Construction and Building Materials*, vol. 191, pp. 270-280, 2018.
- [4] S. Li, Q. J. Yu, and J. Wei, "Effect of molecular structure of polycarboxylate water reducers on hydration of cement," *Journal of the Chinese Ceramic Society*, vol. 40, pp. 613-619, 2012.
- [5] F. Dalas, S. Pourchet, A. Nonat, D. Rinaldi, S. Sabio, and M. Mosquet, "Fluidizing efficiency of comb-like superplasticizers: the effect of the anionic function, the side chain

- length and the grafting degree," *Cement and Concrete Research*, vol. 71, pp. 115–123, 2015.
- [6] T. Yang, X. Yao, Z. Zhang, and H. Wang, "Mechanical property and structure of alkali-activated fly ash and slag blends," *Journal of Sustainable Cement-Based Materials*, vol. 1, no. 4, pp. 167–178, 2012.
  - [7] J. Plank, H. Li, M. Ilg et al., "A microstructural analysis of isoprenol ether-based polycarboxylates and the impact of structural motifs on the dispersing effectiveness," *Cement and Concrete Research*, vol. 84, pp. 20–29, 2016.
  - [8] X. Liu, Z. Wang, J. Zhu et al., "Synthesis, characterization and performance of a polycarboxylate superplasticizer with amide structure," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 448, pp. 119–129, 2014.
  - [9] B. Yu, Z. Zeng, Q. Ren, Y. Chen, M. Liang, and H. Zou, "Study on the performance of polycarboxylate-based superplasticizers synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization," *Journal of Molecular Structure*, vol. 1120, pp. 171–179, 2016.
  - [10] A. Lange and J. Plank, "Contribution of non-adsorbing polymers to cement dispersion," *Cement and Concrete Research*, vol. 79, pp. 131–136, 2016.
  - [11] K. Poellmann, A. Strasser, and S. Mueller, "Hydroxy-functional copolymerizable polyalkylene glycol macromonomers, their preparation and use," US Patent 20080097042A1, 2008.
  - [12] M. Kinoshita and S. Tamaki, "Method of producing allyl-ether ester monomers for production of cement dispersants," EP Patent 1302457A2, 2005.
  - [13] Y. Keiji and K. Takafumi, "Process for producing alpha, beta-unsaturated carboxylic acid esters and catalyst for use in such process," EP Patent 1123915A1, 2004.
  - [14] Z. Wang, Z. C. Lu, F. Lu, L. Xiao, and H. Q. Li, "Effect of backbone length on properties of comb-shaped structure polycarboxylate superplasticizers," *Journal of the Chinese Ceramic Society*, vol. 41, no. 11, pp. 1534–1539, 2013.
  - [15] C. Z. Li, *Study on the Synthesis and Properties of Novel Polycarboxylate-Type High Range Water-Reducers*, Tsinghua University, Beijing, China, 2004.
  - [16] C.-Z. Li, N.-Q. Feng, Y.-D. Li, and R.-J. Chen, "Effects of polyethylene oxide chains on the performance of polycarboxylate-type water-reducers," *Cement and Concrete Research*, vol. 35, no. 5, pp. 867–873, 2005.
  - [17] F. Winnefeld, S. Becker, J. Pakusch, and T. Götz, "Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems," *Cement and Concrete Composites*, vol. 29, no. 4, pp. 251–262, 2007.
  - [18] R. J. Flatt and Y. F. Houst, "A simplified view on chemical effects perturbing the action of superplasticizers," *Cement and Concrete Research*, vol. 31, no. 8, pp. 1169–1176, 2001.
  - [19] K. R. Duan, Y. L. Gao, H. Yao et al., "Comparison of performances of early aged pre-vibrated cement-stabilized macadam formed by different compactions," *Construction and Building Materials*, vol. 239, Article ID 117682, 2020.
  - [20] Z. Feng, F. Kong, Z. Deng, L. F. Fu, and M. H. Yu, "Study on the preparation of amide type polycarboxylate superplasticizer," *Concrete*, vol. 30, pp. 64–67, 2014.
  - [21] W. Wang, "Synthesis of macromonomer polyethylene glycol monoethyl ether methacrylate by transesterification," *Petrochemical Technology*, vol. 37, no. 8, pp. 797–800, 2008.
  - [22] L. W. Hao, "Synthesis of high dispersing polycarboxylic high performance water reducer," M.S. thesis, Beijing University of Technology, Beijing, China, 2007.
  - [23] L. H. Zhang, "Study on synthesis and dispersion performance of polycarboxylic superplasticizers," M.S. thesis, Hebei University of Technology, Tianjin, China, 2007.
  - [24] X. Huang, "Research on synthesis and slump retention properties of polyether graft polycarboxylate superplasticizer," M.S. thesis, South China University of Technology, Guangzhou, China, 2012.
  - [25] Z. P. Sun and Z. Lei, "Study of synthesis of polycarboxylate based superplasticizer," *Journal of Building Materials*, vol. 12, pp. 127–120, 2009.
  - [26] Q. Ran, P. Somasundaran, C. Miao, J. Liu, S. Wu, and J. Shen, "Effect of the length of the side chains of comb-like copolymer dispersants on dispersion and rheological properties of concentrated cement suspensions," *Journal of Colloid and Interface Science*, vol. 336, no. 2, pp. 624–633, 2009.
  - [27] J. Plank, K. Pöllmann, N. Zouaoui, P. R. Andres, and C. Schaefer, "Synthesis and performance of methacrylic ester based polycarboxylate superplasticizers possessing hydroxy terminated poly (ethylene glycol) side chains," *Cement and Concrete Research*, vol. 38, no. 10, pp. 1210–1216, 2008.
  - [28] K. Yamada, T. Takahashi, S. Hanehara, and M. Matsuhsa, "Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer," *Cement and Concrete Research*, vol. 30, no. 2, pp. 197–207, 2000.
  - [29] L. L. Zhu, E. J. Feng, Z. H. Xu, and S. Yan, "Synthesis of high performance polyether grafted polycarboxylate based superplasticizer," *Journal of Nanjing University of Technology*, 2010.
  - [30] B. Felekoğlu and H. Sarıkahya, "Effect of chemical structure of polycarboxylate-based superplasticizers on workability retention of self-compacting concrete," *Construction and Building Materials*, vol. 22, no. 9, pp. 1972–1980, 2008.
  - [31] Z. P. Sun and X. R. Huang, "Study on allyl polyethylene glycol based polycarboxylate superplasticizer," *Journal of Building Materials*, vol. 12, pp. 407–412, 2009.
  - [32] S. H. Lv, F. Li, W. Fei, and L. Gang, "Synthesis and properties of new polycarboxylic acid type superplasticizer," *Journal of Building Materials*, vol. 11, pp. 515–521, 2008.
  - [33] Z. P. Sun, X. Q. Wu, H. H. Huang, K. P. Zheng, J. Yang, and D. M. Ye, "A new kind of synthesis and applied method of polycarboxylate superplasticizer with reduction function," CN Patent 201010102093, 2010.
  - [34] G. J. Wang and H. Feng, "Research of preparation in polycarboxylate superplasticizer using after-vinegar method," *New Building Materials*, vol. 4, pp. 44–49, 2006.
  - [35] L. Ferrari, J. Kaufmann, F. Winnefeld, and J. Plank, "Multi-method approach to study influence of superplasticizers on cement suspensions," *Cement and Concrete Research*, vol. 41, no. 10, pp. 1058–1066, 2011.
  - [36] Y. Yang, "Synthesis and performance of polycarboxylate superplasticizers via water-soluble azo initiator," M.S. thesis, North University of China, Taiyuan, China, 2014.
  - [37] C. Yu, "Study on synthesis and properties of polycarboxylic acid type high performance water-reducer with APEG," M.S. thesis, Chongqing University, Chongqing, China, 2008.
  - [38] Q. Du, "Study on early strength performance of polycarboxylate superplasticizer with mechanism," M.S. thesis, Wuhan University of Technology, Wuhan, China, 2012.
  - [39] J. B. Hu, "Synthesis of ether-type polycarboxylate superplasticizer and research on hydration regulation of C3A-CaSO<sub>4</sub>·2H<sub>2</sub>O system," M.S. thesis, Wuhan University of Technology, Wuhan, China, 2012.
  - [40] D. Hamada, T. Hamai, M. Shimoda, M. Shonaka, and H. Takahashi, "Development of new superplasticizer

- providing ultimate workability," *American Concrete Institute*, vol. 239, pp. 31–50, 2006.
- [41] E. T. Shawl, "Carboxylic acid group-containing additives for cement, cement compositions containing the additives, and manufacture of the additives," US Patent 5670578, 1997.
- [42] H.-Y. Cho and J.-M. Suh, "Effects of the synthetic conditions of poly{carboxylate-g-(ethylene glycol) methyl ether} on the dispersibility in cement paste," *Cement and Concrete Research*, vol. 35, no. 5, pp. 891–899, 2005.
- [43] L. N. Wang, F. Q. Zhang, W. G. Li, L. Ren, and L. X. Wang, "Preparation and diffusion properties of polycarboxylic superplasticizers," *Concrete*, vol. 1, pp. 104–106, 2006.
- [44] L. X. Zeng, "Study on synthesis process and performance of polyether kind polycarboxylic acid water reducing agent," *New Building Materials*, vol. 5, pp. 48–50, 2008.
- [45] A. Büyükyavaş, G. Tuzcu, and L. Aras, "Synthesis of copolymers of methoxy polyethylene glycol acrylate and 2-acrylamido-2-methyl-1-propanesulfonic acid: its characterization and application as superplasticizer in concrete," *Cement and Concrete Research*, vol. 39, no. 7, pp. 629–635, 2009.
- [46] T. Hirata, T. Yuasa, T. Uno, K. Nagare, H. Tahara, and S. Iwai, "Cement composition," US Patent 5925184A, 1999.
- [47] D. J. Adams, S. H. Rogers, and P. Schuetz, "The effect of PEO block lengths on the size and stability of complex coacervate core micelles," *Journal of Colloid and Interface Science*, vol. 322, no. 2, pp. 448–456, 2008.
- [48] Z. Y. Zhang, Q. P. Ran, Y. Yang, Y. Mao, and D. Zhou, "Study on preparation and performance of polymaleic water reducer based on allyl polyethylene glycol," *New Building Materials*, vol. 6, pp. 40–43, 2011.
- [49] X. B. Hu, "Research on synthesis optimization test of polycarboxylate superplasticizer," M.S. thesis, Chongqing University, Chongqing, China, 2010.
- [50] C. Y. Liu, "Research on synthesis and performance of polycarboxylate superplasticizer with slump loss resistance," M.S. thesis, Shanxi University, Taiyuan, China, 2012.
- [51] C. F. Fu, "Study on molecular structure and slump retention mechanism of polycarboxylate superplasticizer," M.S. thesis, Wuhan University of Technology, Wuhan, China, 2012.
- [52] Z. J. Jiang, Y. H. Fang, X. Q. Guo, T. X. Lin, M. Q. Guan, and R. L. You, "Preparation of an extra high-concentration polycarboxylate superplasticizer," *New Building Materials*, vol. 3, pp. 29–31, 2013.
- [53] Y. Yang, Q. P. Ran, J. P. Liu, Z. Y. Zhang, and C. W. Miao, "Synthesis of comb-branched polycarboxylate superplasticizers," *New Building Materials*, vol. 7, pp. 54–56, 2011.
- [54] M. Q. Guan, "The conventional temperature synthesis of high performance polycarboxylates superplasticizer by the oxidation-reduction composite system," *New Building Materials*, vol. 8, pp. 64–67, 2014.
- [55] L. C. Guo, T. Y. Hao, X. M. Ren et al., "A new kind of synthesis method of polycarboxylate superplasticizer at room temperature," CN Patent 101775107, 2010.
- [56] Z. M. Wang, H. Wu, X. Liu et al., "A new kind of synthesis method of polycarboxylate superplasticizer at room temperature," CN Patent 101974135, 2011.
- [57] C. J. Shi, "A new kind of synthesis method of polycarboxylate superplasticizer," CN Patent 101906193, 2010.
- [58] F. L. Zheng, X. L. Chen, Z. D. Lan et al., "Synthesis of ether type polycarboxylate superplasticizer in redox initiator system," in *Proceedings of the Conference on the Production Technology and Application of Concrete Admixture*, pp. 97–101, Jiangmen, China, 2012.
- [59] C. L. Wu, W. Zhang, W. J. Xun, D. S. Xin, and Y. S. Wang, "Study on synthesis of poly-carboxylic acid water-reducing agent under low temperature," *Contemporary Chemical Industry*, vol. 40, no. 4, pp. 359–360, 2011.
- [60] Y. L. Yu, J. P. Liu, L. L. Huo et al., "Study on polymerization process and performance of poly-carboxylic acid water-reducing agent without heat resource," *Concrete*, vol. 11, pp. 84–86, 2014.
- [61] K. Zhu, X. J. Fu, Z. Xia, Z. Zhang, and H. Zhao, "Study on synthesis of polycarboxylic acid water-reducing agent under normal atmospheric temperature," *Concrete*, vol. 33, pp. 59–61, 2013.
- [62] E. Sakai, J. K. Kang, and M. Daimon, "Action mechanisms of comb-type superplasticizers containing grafted polyethylene oxide chains," *American Concrete Institute Special Publication*, vol. 195, pp. 75–90, 2000.
- [63] M. Kinoshita, T. Nawa, M. Lida, and H. Lchiboji, "Effect of chemical structure on fluidizing mechanism of concrete superplasticizer containing polyethylene oxide graft chains," *American Concrete Institute Special Publication*, vol. 195, pp. 163–180, 2000.
- [64] S. Honda, T. Hara, and H. Koyata, "Dispersant composition for cement having excellent property in inhibition of slump-loss," US Patent 5432212A, 1995.
- [65] L. Lei and J. Plank, "Synthesis, working mechanism and effectiveness of a novel cycloaliphatic superplasticizer for concrete," *Cement and Concrete Research*, vol. 42, no. 1, pp. 118–123, 2012.
- [66] J. Plank and H. Bian, "Method to assess the quality of casein used as superplasticizer in self-levelling compounds," *Cement and Concrete Research*, vol. 40, no. 5, pp. 710–715, 2010.
- [67] J. Plank and B. Sachsenhauser, "Experimental determination of the effective anionic charge density of polycarboxylate superplasticizers in cement pore solution," *Cement and Concrete Research*, vol. 39, no. 1, pp. 1–5, 2009.
- [68] J. Plank and C. Winter, "Competitive adsorption between superplasticizer and retarder molecules on mineral binder surface," *Cement and Concrete Research*, vol. 38, no. 5, pp. 599–605, 2008.
- [69] H. Uchikawa, D. Sawaki, and S. Hanehara, "Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement paste," *Cement and Concrete Research*, vol. 25, no. 2, pp. 353–364, 1995.
- [70] H. Uchikawa, S. Hanehara, and D. Sawaki, "The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture," *Cement and Concrete Research*, vol. 27, no. 1, pp. 37–50, 1997.
- [71] S. Li, Z. Wen, and H. Wang, "Synthesis of polycarboxylate-type superplasticizer and its effects on the performance of cement-based materials," *Journal of the Chinese Ceramic Society*, vol. 36, no. 7, pp. 884–889, 2008.
- [72] X. Kong, S. Hou, and Z. H. Shi, "Influences of functional monomers on performance of polycarboxylate superplasticizers," *Journal of Building Materials*, vol. 17, no. 1, pp. 1–8, 2014.
- [73] Z. M. Wang, Z. C. Lu, F. Lu, and H. Q. Li, "Effect of side chain density of comb-shaped structure on performance of polycarboxylate superplasticizer," *Journal of the Chinese Ceramic Society*, vol. 40, no. 11, pp. 1570–1575, 2012.
- [74] Q. P. Ran, C. W. Miao, J. P. Liu, S. Yan, and Y. Mao, "Action mechanism and effect of side chain length of comb-like copolymer dispersant on dispersion of cement paste," *Journal of the Chinese Ceramic Society*, vol. 37, no. 7, pp. 1153–1159, 2009.

- [75] J. Zhang, L. Ding, F. Li, and J. Peng, "Recycled aggregates from construction and demolition wastes as alternative filling materials for highway subgrades in China," *Journal of Cleaner Production*, vol. 255, Article ID 120223, 2020.
- [76] J. Zhang, F. Gu, and Y. Zhang, "Use of building-related construction and demolition wastes in highway embankment: laboratory and field evaluations," *Journal of Cleaner Production*, vol. 230, pp. 1051–1060, 2019.
- [77] L. D. Zhang, "Preparation and properties of maleic acid-type superplasticizers," M.S. thesis, Shaanxi University of Science & Technology, Xi'an, China, 2013.
- [78] M. Zhang, B. Duan, J. Jia, and H. Wang, "Research on synthesis of a new type of polycarboxylate superplasticizer," *New Building Materials*, vol. 3, pp. 84–87, 2010.
- [79] C. W. Miao, Q. P. Ran, J. Hong, J. Xu, and D. Zhou, "Present situation and developmental trends of polycarboxylate-type superplasticizers," *Materials China*, vol. 28, no. 11, pp. 36–45, 2009.
- [80] L. F. Pang, X. Q. Li, Y. H. Wei, and X. Z. Zhang, "Superplasticizer synthesis and applicable performance of polycarboxylic acid concrete," *Concrete*, vol. 10, pp. 68–70, 2004.
- [81] V. Mechtcherine, "Fracture mechanical behavior of concrete and the condition of its fracture surface," *Cement and Concrete Research*, vol. 39, no. 7, pp. 620–628, 2009.
- [82] J. Plank and B. Yu, "Preparation of hydrocalumite-based nanocomposites using polycarboxylate comb polymers possessing high grafting density as interlayer spacers," *Applied Clay Science*, vol. 47, no. 3-4, pp. 378–383, 2010.
- [83] J. Plank, Z. Dai, and P. R. Andres, "Preparation and characterization of new Ca-Al-polycarboxylate layered double hydroxides," *Materials Letters*, vol. 60, no. 29-30, pp. 3614–3617, 2006.
- [84] J. A. Lewis, H. Matsuyama, G. Kirby, S. Morissette, and J. F. Young, "Polelectrolyte effects on the rheological properties of concentrated cement suspensions," *Journal of the American Ceramic Society*, vol. 83, pp. 1905–1913, 2000.
- [85] J. Plank and C. Hirsch, "Impact of zeta potential of early cement hydration phases on superplasticizer adsorption," *Cement and Concrete Research*, vol. 37, no. 4, pp. 537–542, 2007.
- [86] B. Jiang, S. Zhou, H. Ji, B. Liao, and H. Pang, "Dispersion and rheological properties of ceramic suspensions using linear polyacrylate copolymers with carboxylic groups as superplasticizer," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 396, pp. 310–316, 2012.
- [87] W. Fan, F. Stoffelbach, J. Rieger et al., "A new class of organosilane-modified polycarboxylate superplasticizers with low sulfate sensitivity," *Cement and Concrete Research*, vol. 42, no. 1, pp. 166–172, 2012.
- [88] O. Burgos-Montes, M. Palacios, P. Rivilla, and F. Puertas, "Compatibility between superplasticizer admixtures and cements with mineral additions," *Construction and Building Materials*, vol. 31, pp. 300–309, 2012.
- [89] M. F. Chen, H. J. Zhang, J. H. Peng et al., "Synthesis and performance of polycarboxylic water reducing agent," *Chemical Materials for Construction*, vol. 21, no. 2, pp. 54–55, 2005.
- [90] T. M. Vickers, S. A. Farrington, J. R. Bury, and L. E. Brower, "Influence of dispersant structure and mixing speed on concrete slump retention," *Cement and Concrete Research*, vol. 35, no. 10, pp. 1882–1890, 2005.
- [91] L. C. Zhi, Y. D. Li, and F. N. Qian, "Study on the synthesis technology of polycarboxylic type water-reducer," *Journal of Building Materials*, vol. 5, pp. 326–330, 2002.
- [92] W. Guo, N. Sun, J. Qin et al., "Synthesis and properties of an amphoteric polycarboxylic acid-based superplasticizer used in sulfoaluminate cement," *Journal of Applied Polymer Science*, vol. 125, no. 1, pp. 283–290, 2012.
- [93] A. Amin, H. H. M. Darweesh, A. M. Ramadan, S. M. M. Morsi, and M. M. H. Ayoub, "Employing of some hyperbranched polyesteramides as new polymeric admixtures for cement," *Journal of Applied Polymer Science*, vol. 121, no. 1, pp. 309–320, 2011.
- [94] Y. F. Zhi, T. W. Song, F. Wu, W. Wang, D. M. Wang, and Q. B. Wang, "Study on the hyperbranched carboxyl terminated polycarboxylate superplasticizer synthetic process and performance," *Ready-Mixed Concrete*, vol. 21, pp. 43–48, 2011.
- [95] C. Shou, X. U. Lei, D. Jiang, B. Liu, and L. Xu, "Study of hyperbranched star polycarboxylate superplasticizer and its application in sulphoaluminate cement," *New Building Materials*, vol. 11, pp. 18–23, 2011.