Synthesis and Application of Polycarboxylate Superplasticizer with Viscosity-reducing and Low Shrinkage Capability

Shan-Shan QIAN\textsuperscript{1,a,*}, Hai-Dong JIANG\textsuperscript{1,b}, Bei DING\textsuperscript{1,c}, Yi WANG\textsuperscript{1,d}, Chun-Yang ZHENG\textsuperscript{1,e}

\textsuperscript{1}No. 22, Huixin Road, Zhongshan Science and Technology Park, Nanjing, China
\textsuperscript{a}arltqss@163.com, \textsuperscript{b}arltjhd@163.com, \textsuperscript{c}arltdb@163.com, \textsuperscript{d}arltwy@163.com, \textsuperscript{e}aritzcy@163.com

*Corresponding author

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Abstract. A low shrinkage and viscosity-reducing type polycarboxylate superplasticizer was synthesized with maleic anhydride (MAH), diethylene glycol monobutyl ether (DGBE) and methoxypoly (ethylene glycol) methacrylate (MPEG\textsubscript{n}MA). The surface tension, early shrinkage of concrete, cement paste and application performance in concrete (slump spread, T\textsubscript{50}, V-funnel) were measured. The results show that the polycarboxylate superplasticizer we prepared has good low shrinkage and excellent viscosity-reducing capability for concrete.

Introduction

With the rapid development of construction and material industries, modern buildings tend to become high-level, light-weight and large-span. High grade concrete is more and more widely used in infrastructures in China owing to its characteristics such as high overall strength and light weight\textsuperscript{[1,2]}. In order to achieve high strength concrete or ultra-high strength concrete, large amounts of cementing materials and low water-cement ratio have to be used. This will lead to problems of high viscosity and low fluidity of the fresh concrete, and further lead to difficulties in construction. The problems of high viscosity and shrinkage of ultra-high performance concrete are especially serious in China, resulting in frequent engineering accidents\textsuperscript{[3]}. At present, reducing the viscosity of high strength concrete is mainly through improving the mixing amount of superplasticizer and optimizing the particle size distribution by superior ultrafine powder\textsuperscript{[4]}. For reducing the viscosity of concrete by improving the mixing amount of superplasticizer, the following problems may occur. Firstly, the costs will increase; secondly, excessive retarded setting will appear, and then causing a long cycle for removing moulds; thirdly, problems, such as bleeding, grilled bottom and others, may cause some difficulties during construction\textsuperscript{[5]}. Although there are many studies concerning the effects of optimizing the particle size distribution of superior ultrafine powders on reducing concrete viscosity, the method has some limitations. The fluidity of fresh concrete mainly depends on strong adsorption and dispersion of superplasticizer, so the optimization of particle size distribution cannot fundamentally solve practical problems\textsuperscript{[6,7]}. These methods, for example, mixing fiber, shrinkage reducing agent and expansion agent in the concrete, are mainly used to reduce the shrinkage of concrete. However, all these methods have limitations e.g. too low dosage of expansion agent, so the desired effects cannot be achieved; but if the dosage is too high, it may lead to the appearance of cracks because of excessive expansion, or make the existing
cracks become larger\[8\]; fiber has some effects on reducing shrinkage, and the cost is low, but it has poor compatibility with concrete; some shrinkage reducing agents on the market have a good reducing shrinkage effect, but both the dosage and price are high, so that the concrete cost is greatly increased\[9\]. Consequently, developing polycarboxylate superplasticizer with viscosity-reducing and low shrinkage capability has great practical significance.

In this paper, in order to solve the problems such as high viscosity, low flow velocity and great shrinkage, we synthesized the polycarboxylate superplasticizer with viscosity-reducing and low shrinkage capability by selecting monomers with different structures and functions, designing special molecular structure of the polycarboxylate superplasticizer, optimizing the polymerization degree of the main chain, the length of the side chain and types of functional groups to realize the high performance of polycarboxylate superplasticizer. In the present paper, methoxypoly (ethylene glycol) methacrylate macromonomer, maleic anhydride monomer and diethylene glycol monobutyl ether were used as raw materials. Based on the redox initiation system and the design of molecular structure, diethylene glycol monobutyl ether with the function of reducing shrinkage was grafted on the main chain of maleic anhydride, according to the molecular structure and function mechanism of polycarboxylate superplasticizer. Then, a polycarboxylate superplasticizer with viscosity-reducing, low shrinkage capability and comb-type molecular structure was synthesized. Besides, we also designed the molecular structure and optimized the synthesis process. Therefore, it can play a role in reducing the shrinkage ratio and the viscosity of concrete, so as to improve the rheological properties and working performance to meet engineering requirements.

**Raw Materials and Instrument**

**Raw Materials**

The raw materials used include: methoxypoly(ethylene glycol) methacrylate macromonomer (MPEGnMA), polyethylene glycol monomethyl ether ester with molecular weight of 750, 2000, 3000 (shown in MPEG16MA, MPEG45MA and MPEG67MA respectively), available from Liaoning Kelong Fine Chemical Co., Ltd. Tackifier: cellulose ether MHPC500PF, available from Shanghai Greenchem Trading Co., Ltd. diethylene glycol monobutyl ether, maleic anhydride (MD), sodium methylallylsulfonate (SMAS), hydrogen peroxide, sodium hydroxide, K12, AR, available from Sinopharm Chemical Reagent Co., Ltd.; vitamin C, commercially available.

**Experimental Materials**

Cement: P•O 42.5 reference cement. Please see Table 1 for its chemical and mineral compositions.

| SiO2 | A2O3 | F2O3 | CaO | MgO | SO3 | N2Oeq | f-CaO | C3S | C2S | C3A | C4AF |
|------|------|------|-----|-----|-----|-------|------|-----|-----|-----|-------|
| 22.92| 4.38 | 2.88 | 66.14| 1.94| 0.32| 0.73   | 0.62 | 58.59| 21.57| 6.59| 8.69 |

The medium sand has a fineness modulus M=2.7, density of 2551kg/m$^3$ and bulk density of 1461kg/m$^3$.

The macadam is 5~20 mm continuous grading macadam. Wherein the percentage of 5~10 mm is 40%, that of 10~20 mm is 60%, that of flat-elongated particles is less than 5%, the
close void fraction is less than 40%, the clay content is less than 0.5%, the density is 2630kg/m³ and the bulk density is 1540 kg/m³.

Tap water was used.

**Main Instrument**

HH-S1 thermostatic water bath, Jintan Medical Instrument Factory; JJ-1A electric stirrer, Jintan Ronghua Instrument Manufacture Co., Ltd.; NJ-160A cement paste mixer, Wuxi Jianyi Instrument & Machinery Co., Ltd.; HJW60 forced mixer for concrete test, Wuxi Jianyi Instrument & Machinery Co., Ltd.; WHY-2000 computer control pressure testing machine, Shanghai Hualong Test Instruments Corporation.

**Synthesis of P(MD-MPEGₙMA)ₘ**

1. Synthesis of functional monomer(MD) with low shrinkage capability: diethylene glycol monobutyl ether(DGBG), maleic anhydrite(MAH) and the catalyst were added into a three-neck flask and reacted at 100°C~140°C for 5 h. After vacuum distillation and cooling, the functional monomer was obtained for further use.

2. Synthesis of P(MD-MPEGₙMA)ₘ: hydrogen peroxide, SMAS and water were weighed and added into the three-neck flask with macromonomer MPEGₙMA, and then stirred and heated for 15 min in a water bath. A, B components were dropped simultaneously, in which Component A is the aqueous solution of monomer with low shrinkage capacity and Component B is Vc aqueous solution. And 3 h and 3.5 h were used respectively to complete the addition, and they were reacted for 1 h under incubated conditions. After cooling, NaOH solution with concentration of 40% was added to adjust the pH of reactants to neutral. The obtained polycarboxylate superplasticizer mother liquid was placed in a dialysis bag (MWCO 5000), in which the volume of superplasticizer is about one-fifth of the capacity of the dialysis bag. The water was refreshed for 4~6 times a day. After dialysis for a week, the desired P(MD-MPEGₙMA)ₘ could be obtained.

**Characterization**

**Gel permeation chromatography (GPC) analysis.** Waters 1515 gel permeation chromatograph was used to test the molecular weight and its distribution of the synthesized samples. The mobile phase is 0.1 mol.L⁻¹ NaNO₃ solution, the flow rate is 1.0 ml/min, and the stationary phase is gelatinous porous filler.

**Surface tension test.** According to GB/T8077-2000, the surface tension test was conducted, in order to test the surface tension of the solution mixed with polycarboxylate superplasticizer by OCA40 Micro surface contact angle tester of Dataphysics with measurement range of 0.01~2000mN/m, measurement accuracy of ±0.01mN/m and the measurement range of the contact angle of 0-180°.

**Shrinkage of concrete.** The test was conducted by the contact method of the shrinkage test according to GB/T50082-2009 Standard for Test Methods of Long-term Performance and Durability of Ordinary Concrete. PVC tube with a diameter of 100 mm, height of 515 mm was used as a mold to shape the concrete samples. After shaping, the sample was immediately placed into an environment with temperature of (20±2)°C and relative humidity of (60±5)%. Putting a small piece of glass on the sample, the probe of deformation automatic acquisition instrument was used to press the glass sheet gently. The shrinkage automatic acquisition instrument was started until the initial setting of the concrete was realized, to collect the shrinkage value within 72 h.
Cement paste test. The fluidity and maintaining performance of cement paste were conducted according to GB 8077-2000 Methods for Testing Uniformity of Concrete Admixture. The water-cement ratio was 0.29 and the mixing amount of superplasticizer was 0.12%.

Concrete test. The tests of concrete expansion degree, T50 and V funnel were conducted according to related requirements of CECS203-2006 Technical Specifications for Self Compacting Concrete Application.

Results and discussion

Molecular weight and its distribution of P(MD-MPEG_nMA)_m

In order to study the effects of average molecular weight, side-chain length and content of methacrylic acid in viscosity-reducing superplasticizer on the viscosity of concrete, the following ones were designed: 1) P(MD_{3.5}-MPEG_{16}MA)_{5,}, P(MD_{4}-MPEG_{16}MA)_{9} and P(MD_{4.5}-MPEG_{16}MA)_{12} synthesized with the same polyether side chain MPEG_{16}MA and different MD:MPEG_{16}MA ratios; 2) P(MD_{4}-MPEG_{16}MA)_{9}, P(MD_{4}-MPEG_{45}MA)_{9} and P(MD_{4}-MPEG_{67}MA)_{9} synthesized with different polyether side chains of MPEG_{16}MA, MPEG_{45}MA and MPEG_{67}MA and the same MD:MPEG_{n}MA ratio. The results are shown in Table 2 and Fig. 2.

Table 2. The GPC results of superplasticizers P(MD-MPEG_{n}MA)_m.

| Entry | Feed ratio (MD:MPEG_{n}MA) | Superplasticizer P(MD-MPEG_{n}MA)_m | GPC results |
|-------|-----------------------------|--------------------------------------|-------------|
|       |                             |                                      | M_n (g∙mol^{-1}) | M_w (g∙mol^{-1}) | PDI |
| A     | 3.5:1                       | P(MD_{3.5}-MPEG_{16}MA)_{5}          | 5500         | 6800           | 1.25 |
| B     | 4:1                         | P(MD_{4}-MPEG_{16}MA)_{9}           | 10600        | 15200          | 1.42 |
| C     | 4.5:1                       | P(MD_{4.5}-MPEG_{16}MA)_{12}        | 15200        | 21100          | 1.38 |
| D     | 4:1                         | P(MD_{4}-MPEG_{45}MA)_{9}           | 22000        | 31200          | 1.41 |
| E     | 4.1                         | P(MD_{4}-MPEG_{67}MA)_{9}           | 30100        | 41800          | 1.39 |

Figure 1. GPC trace of P(MD-MPEG_{n}MA)_m.
The values of GPC in Table 2 correspond to the corresponding peak in Fig. 1. As can be seen from Fig. 1, the GPC spectrums of synthesized products mainly concentrate in a very narrow range, meaning that they all have desired structures.

**The Surface Tension Test of P(MD-MPEG\_n\_MA)\_m in Water Solution**

Wilhelmy method was used to determine the surface tensions of solutions mixed with different concentrations of the low shrinkage and high slump polycarboxylate superplasticizer, namely 1.0%, 2.0%, 3.0%, 4.0%, 5.0%, 6.0%, 7.0%, 8.0%, 9.0% and 10%. The surface tension of the same solution was measured for 3 times and the results were averaged.

![Surface tension vs Concentration](image)

Figure 2. The surface tension of P(MD-MPEG\_n\_MA)\_m in different concentration.

From Fig.2, it can be seen that the surface tension of pure water without additives is 72.47 mN/m. When the concentration of P(MD4-MPEG16MA)\_9 is 10%, the surface tension of the solution is 30.56 mN/m. It shows that the surface tension reduces significantly with the addition of P(MD-MPEG\_n\_MA)\_m, which has important effects on improving cement particles' dispersity and maintaining dispersion performance. From the overall changing trend in Fig. 2, we can see that with an increase in concentration of polycarboxylate superplasticizer, the surface tension decreases in the following order: P(MD4-MPEG16MA)\_9 > P(MD4.5-MPEG16MA)\_12 > P(MD3.5-MPEG16MA)\_5 > P(MD4-MPEG45MA)\_9 > P(MD4-MPEG67MA)\_9. P(MD4-MPEG16MA)\_9 has a long main chain, short side chain, low molecular weight and small steric hindrance. Association of the hydrophobic groups in this comb structure occurs in water solution, so that the hydrophobic groups gather and shrink together and wrap the hydrophilic structure to make them in the interior. Therefore, the surface tension reduces with increase in the concentration of viscosity-reducing superplasticizer. For P(MD4.5-MPEG16MA)\_12 has a long main chain, the hydrogen atom of carboxylic acid group in the main chain is easy to associate with the oxygen atom in the branch, so the interaction force between macromolecular chains increases and also the degree of aggregation. This will lead to an increase in solution viscosity and surface tension of the synthesized polycarboxylate superplasticizer. While for P(MD4-MPEG67MA)\_9, the steric hindrance provided by MPEG67MA in branches is much larger than that of MPEG45MA and MPEG16MA, so the surface tension slowly decreases with increasing concentrations of superplasticizer. The low
surface tension of the viscosity-reducing polycarboxylate superplasticizer can reduce the solid-liquid interface energy of cement particles. In addition, it is easy to form many micro-bubbles in the fresh concrete. The micro-bubbles can isolate the cement particles and decrease the adsorption of cement particles on polycarboxylate superplasticizer, to make the cement particles disperse and stably disperse.

**Concrete shrinkage**

The shrinkage results from the early age to 72 h of concrete samples are shown in Fig. 3. The 72 h shrinkage values of concrete mixed with superplasticizer P(MD₄-MPEG₄5MA)₉ and P(MD₄-MPEG₆7MA)₉ are respectively 240×10⁻⁶m/m and 295×10⁻⁶m/m, being 77.7% and 96.4% of that of the reference concrete (blank sample). The 72 h shrinkage value of concrete mixed with P(MD₄-MPEG₄5MA)₉ decreases by 18.7% than that of P(MD₄-MPEG₆7MA)₉, which can effectively ensure the engineering safety.

![Figure 3. The result of early age shrinkage of concrete.](image)

The shrinkage value decreases significantly after adding different polycarboxylate superplasticizers with viscosity-reducing and low shrinkage capability, wherein P(MD₄-MPEG₄5MA)₉ decreases the most, and P(MD₄-MPEG₆7MA)₉ the least. This is due to the molecular structure of diethylene glycol monobutyl ether contains hydrophobic group of methyl, which can adjust the hydrophilic lipophilic balance (HLB) value of superplasticizer molecules. Main reasons of decrease in shrinkage values for P(MD-MPEGₙMA)ₙ may be the insertion of monomers with low shrinkage. It can significantly reduce the concrete gas-liquid surface tension, and improve the pore structure of hardened cement paste. Thus the evaporation rate of moisture inside the pores slows down, so the capillary tension generated by dehydration in capillary pores reduces to realize the low shrinkage. The above results are in good agreement with those of surface tension.

**Effects of P(MD-MPEGₙMA)ₙ on Cement Paste Fluidity**

The important reaction parameters, such as average molecular weight, length of side chains and content of maleic anhydrite of P(MD-MPEGₙMA)ₙ, directly determine the initial fluidity and fluidity retention capability of concrete. The results of effects of different P(MD-MPEGₙMA)ₙ on cement paste fluidity are shown in Table 3.
Table 3. Effect of P(MD-MPEG\textsubscript{n}MA\textsubscript{m}) on cement paste fluidity.

| Entry | Superplasticizer P(MD-MPEG\textsubscript{n}MA\textsubscript{m}) | Dosage/\% | Fluidity/mm |
|-------|-----------------|---------|-------------|
|       |                 |         | Initial | 0.5h | 1h |
| A     | P(MD\textsubscript{3.5}-MPEG\textsubscript{16}MA\textsubscript{5}) |         | 203     | 185  | 163 |
| B     | P(MD\textsubscript{4}-MPEG\textsubscript{16}MA\textsubscript{9}) | 0.18   | 230     | 205  | 198 |
| C     | P(MD\textsubscript{4.5}-MPEG\textsubscript{16}MA\textsubscript{12}) |         | 222     | 171  | 148 |
| D     | P(MD\textsubscript{4}-MPEG\textsubscript{45}MA\textsubscript{9}) |         | 220     | 190  | 178 |
| E     | P(MD\textsubscript{4}-MPEG\textsubscript{67}MA\textsubscript{9}) |         | 205     | 170  | 139 |

As can be seen from Table 3, when side chains of superplasticizers have different lengths and the ratio of MD:MPEG\textsubscript{n}MA is 4:1, the initial fluidity and fluidity retention capability of concrete decreases in the following sequence: P(MD\textsubscript{4}-MPEG\textsubscript{16}MA\textsubscript{9}) > P(MD\textsubscript{4}-MPEG\textsubscript{45}MA\textsubscript{9}) > P(MD\textsubscript{4}-MPEG\textsubscript{67}MA\textsubscript{9}). This shows: 1) when the superplasticizer has the same density in the side chain but different lengths, the thickness of the water film formed in concrete becomes thin in theory, so more free water can be released to show excellent initial paste fluidity and fluidity retention capability. 2) When the superplasticizer has the same density in the side chain but different lengths, the water retention performance increases with gradual increase in molecular weight. Owing to the gradual increase in molar weight and side chain, the content of carboxyl increases, and the number of hydrogen bonds which can bound with carboxyl also increases. Hence, more free water can be bound, to affect the performance of dispersion and slump retaining. When the ratio of MD:MPEG\textsubscript{n}MA is 4.5:1 and the side chain length is definite, if the adsorption group is more and the side chain density is lower, lots of adsorption groups of superplasticizer molecules will adsorbe on cement particles. But there is enough repulsion because of the low side chain density, so the general water reduction effect can be obtained. When the ratio of MD:MPEG\textsubscript{n}MA is 3.5:1 and the side chain length is definite, if the adsorption group is less and the side chain density is higher, steric hindrance is difficult to achieve. It is probably due to insufficient number of adsorption group and much high density of side chain. Therefore, the paste fluidity and retention performance is poor.

Effects of P(MD-MPEG\textsubscript{n}MA\textsubscript{m}) on fresh concrete application performance

In accordance with JGJ 55-2011 Specification for Mix Proportion Design of Ordinary Concrete and JGJ/T 283-2012 Technical Specifications for Self Compacting Concrete Application, the calculation of concrete mix proportion and tests are conducted.

Table 4. Mix proportion of SCC for determining the dosage of P(MD-MPEG\textsubscript{n}MA\textsubscript{m})/kg/m\textsuperscript{3}.

| Entry | Cement | Sand | Coarse aggregate | P(MD-MPEG\textsubscript{n}MA\textsubscript{m}) | VEA | Air entraining agent | Water |
|-------|--------|------|------------------|---------------------------------|-----|---------------------|-------|
| 1     | 520    | 826  | 894              | 3.12                            | 1.04| 0.052               | 165   |
| 2     | 520    | 826  | 894              | 4.16                            | 1.04| 0.052               | 165   |
| 3     | 520    | 826  | 894              | 5.20                            | 1.04| 0.052               | 165   |
| 4     | 520    | 826  | 894              | 6.24                            | 1.04| 0.052               | 165   |
In this test, the amount of cement is 520 kg/m\(^3\) and the sand percentage is 48%. The amounts of superplasticizer used in this test are respectively 0.6%, 0.8%, 1.0% and 1.2% of the cement mass. The mix proportion is shown in Table 4, and the results are listed in Table 5.

Table 5. Influence of the dosage of P(MD-MPEG\(_n\)MA)\(_m\) on the flow ability of SCC.

| Entry | P(MD-MPEG\(_{16}\)MA)\(_5\) | W /% | V funnel /s | T\(_{50}\) /s | Slump flow /mm | Segregation |
|-------|-----------------------------|-----|-------------|--------------|----------------|-------------|
| 1     | P(MD\(_{3.5}\)-MPEG\(_{16}\)MA)\(_5\) | 0.6 | 17 | - | 360 | No |
| 2     | P(MD\(_{3.5}\)-MPEG\(_{16}\)MA)\(_5\) | 0.8 | 13 | 12 | 540 | No |
| 3     | P(MD\(_{3.5}\)-MPEG\(_{16}\)MA)\(_5\) | 1.0 | 11 | 11 | 580 | No |
| 4     | P(MD\(_{3.5}\)-MPEG\(_{16}\)MA)\(_5\) | 1.2 | 10 | 9 | 600 | No |
| 5     | P(MD\(_4\)-MPEG\(_{16}\)MA)\(_9\) | 0.6 | 9 | 10 | 610 | No |
| 6     | P(MD\(_4\)-MPEG\(_{16}\)MA)\(_9\) | 0.8 | 8.2 | 8 | 650 | No |
| 7     | P(MD\(_4\)-MPEG\(_{16}\)MA)\(_9\) | 1.0 | 6.5 | 3.8 | 700 | No |
| 8     | P(MD\(_4\)-MPEG\(_{16}\)MA)\(_9\) | 1.2 | 7.6 | 3.5 | 720 | No |
| 9     | P(MD\(_{4.5}\)-MPEG\(_{16}\)MA)\(_{12}\) | 0.6 | 10 | 8.6 | 610 | No |
| 10    | P(MD\(_{4.5}\)-MPEG\(_{16}\)MA)\(_{12}\) | 0.8 | 8.5 | 7.7 | 630 | No |
| 11    | P(MD\(_{4.5}\)-MPEG\(_{16}\)MA)\(_{12}\) | 1.0 | 7 | 6.9 | 650 | No |
| 12    | P(MD\(_{4.5}\)-MPEG\(_{16}\)MA)\(_{12}\) | 1.2 | 7.8 | 5.4 | 670 | No |
| 13    | P(MD\(_4\)-MPEG\(_{45}\)MA)\(_9\) | 0.6 | 10 | 8 | 600 | No |
| 14    | P(MD\(_4\)-MPEG\(_{45}\)MA)\(_9\) | 0.8 | 9 | 6.5 | 640 | No |
| 15    | P(MD\(_4\)-MPEG\(_{45}\)MA)\(_9\) | 1.0 | 8.9 | 5.2 | 660 | No |
| 16    | P(MD\(_4\)-MPEG\(_{45}\)MA)\(_9\) | 1.2 | 7.6 | 4.7 | 680 | Some mortar separated out |
| 17    | P(MD\(_4\)-MPEG\(_{67}\)MA)\(_9\) | 0.6 | 16 | 13 | 540 | No |
| 18    | P(MD\(_4\)-MPEG\(_{67}\)MA)\(_9\) | 0.8 | 13 | 10 | 570 | No |
| 19    | P(MD\(_4\)-MPEG\(_{67}\)MA)\(_9\) | 1.0 | 10 | 8.6 | 610 | No |
| 20    | P(MD\(_4\)-MPEG\(_{67}\)MA)\(_9\) | 1.2 | 8.6 | 7.5 | 630 | No |

Table 5 shows that, when the dosage of P(MD-MPEG\(_n\)MA)\(_m\) is 0.6%–1.0%, the concrete fluidity increases rapidly as can be seen from results of T\(_{50}\) and V funnel when the dosage is more than 1.0%, the concrete fluidity increases slowly and tends to be a constant; and the segregation phenomenon occurs in the concrete. After comprehensive comparison, the optimum dosage of the superplasticizer is 1.0%. The good fluidity of P(MD-MPEG\(_n\)MA)\(_m\) is due to its own structure. On one hand, the introduction of more hydrophobic groups in its molecular structure reduces the surface tension. For example, that, the introduction of polyether macromolecule with methyl end group in the side chain and diethylene glycol monobutyl ether in the main chain, can reduce its HLB value. The lower HLB value will lead
to decrease in formation of combined water generated by combining diethylene glycol monobutyl ether and water. So a certain amount of water can be released. On the other hand, the performance of superplasticizer depends on the efficiency of single molecule and the number of molecules. The average molecular weight of $P(\text{MD}_{4}\text{-MPEG}_{16}\text{MA})_9$ is only one-third of ordinary polycarboxylate superplasticizer. So it has a higher degree of freedom, and the molecule chain of the superplasticizer can be stretched, to enable a large number of superplasticizer to rapidly adsorb on the surface of concrete. This is why concrete exhibits low viscosity and high fluidity.

**Conclusions**

Based on the principle of molecule design, we synthesized a high performance polycarboxylate superplasticizer with viscosity-reducing and low shrinkage capability by a free radical polymerization method. Through characterizations and study, the main conclusions are shown as follows:

1. Using methoxypoly(ethylene glycol) methacrylate macromonomer (MPEG$_n$MA) and methacrylic acid as main raw materials, the molecular weight and its distribution of the synthesized viscosity-reducing polycarboxylate superplasticizers were characterized by GPC.

2. Those, namely the relationships between the various ratios of maleic anhydride: polyethylene glycol monomethyl ether ester macromonomer (MD:MPEG$_n$MA), the molecular weight of MPEG$_n$MA, the molecular weight and its distribution of polycarboxylate superplasticizer with viscosity-reducing and low shrinkage capability ($P(\text{MD}\text{-MPEG}_{n}\text{MA})_m$) and the low shrinkage and fluidity of concrete, were analyzed.

3. The superplasticizer with viscosity-reducing and low shrinkage capability has better viscosity reducing performance than that of commercially available polycarboxylate superplasticizer. The concrete mixed with this superplasticizer shows excellent low shrinkage and fluidity. It may have a good application prospect.

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