PCEs containing C5 and C6 based PEO side chains: A comparison on the synthesized polymers and the resulting dispersing effectiveness

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Abstract—The reactivity of C5 and C6 based PEO macromonomers in the synthesis of PCE superplasticizers, followed by the dispersing abilities of such PCEs on cement pastes were analysed and compared in this study. It was found that free radical copolymerisation of C5 macromonomers and acrylic acid (AA) produced PCEs with less controlled block copolymers characteristics, which were highly sensitive to reaction conditions such as the rate of polymer additions, etc. This can be attributed to the difference in reactivity constants of the monomers, where AA was highly reactive. The orderness became more dominant when the temperature of synthesis was suitably controlled. The ease in adapting the molecular architecture of C6 based PCEs as compared to C5 based PCEs enabled better prediction of cement dispersing ability, as confirmed by the slump flow tests performed. It was thus shown through this study that using C6 macromonomers, PCE with tailor made architecture could be developed easier than with C5 macromonomers, potentially to adapt to different types of cement on the market.

1. Introduction
In 1981, the polycarboxylate comb polymers was invented, which is an important invention in concrete technology\cite{1}. Superplasticizer (SP) improves a good workability of concrete at a low water to cement ratio, which has some advantages like good frost-thaw resistance, good resistance and high strengths\cite{2}. The ultra-high strength concrete (UHPC) and self-compacting concrete (SCC) can be prepared by the addition of SP. The kinds of SP as following: MPEG-type SP, APEG-type SP (C3), HPEG type SP (C4), TPEG type SP(C5), VPEG SP (C6), organo-silane modified SP, phosphate SP, zwitterionic SP and so on\cite{3-4}. The composition and the structure of the SP influence the rheological properties\cite{5-10}. At present, TPEG-SP has been widely applied in China, but VPEG-SP is noticed by more and more manufacturers as the SP has some excellent features. Scholars have studied the following aspects of VPEG-SP: (1) The synthesis process conditions and dispersion performance of VPEG-SP\cite{11-13}; (2) The effect of VPEG-SP on the viscosity of concrete\cite{14}; (3) The sensitivity of VPEG type PCE to the clay\cite{15-16}. However, there are few reports on the performance of VPEG-SP in SCC concrete.

SCC is completely eliminated the vibration and permits the concrete to flow through congested reinforcement depending on its own weight. The invention of the first SCCs is in late 1980s, Japan\cite{17-19}. Such concrete needs a high slump, good workability, high deformability and a good resistance to segregation\cite{20-21}. The above requirements of SCC are difficult to achieve, so SCC is often limited in the field of precast concretes, although the technology offers many opportunities for the construction
site as well. Using SCC to evaluate the performance of SP is undoubtedly harsh, but it can also be found that the difference in the dispersion performance of SPs on concrete.

2. Research Significance
In this paper, three superplasticizers were synthesized: TPEG-SP widely used in the Chinese market, and two VPEG-SPs synthesized under two different temperature conditions with market potential. Three SPs have been studied for their adaptability to cement and workability in self-compacting concrete. The above work provides technical and theoretical support for the wide application of VPEG-SP.

2.1. Raw materials
The macromonomer 4-hydroxy butylpoly(ethylene glycol) vinyl ether (C6) with Mw=3000 Da was purchased by Liaoning Oxiranchem, Inc.; The macromonomer isoprenyl poly(ethylene glycol) (C5) with Mw=2400 Da was provided by Liaoning Kelong Fine Chemical Co., Ltd.; Pure acrylic acid was supplied by CNPC Lanzhou Petrochemical Company; Deionized water was self-prepared. All chemicals were used as obtained without further purification.

Five kinds of portland cements (P.O 42.5) conforming to Chinese Standard GB175-2007 were adopted in this study. Class II flash ash according to Chinese Standard GB/T1596-2017 was adopted as mineral admixture. The composition of cement was shown in Table 1; Artificial sand with a fineness modulus of 2.70 (as showed in Table 2) were adopted as fine, and natural gravel with a continuous gradation of 5-31.5mm were adopted as coarse aggregates.

### Table 1 The composition of cement

| Cement type | SiO2  | Al2O3 | Fe2O3 | CaO  | SO3  | MgO  | K2O  | Na2O  | Loss |
|-------------|-------|-------|-------|------|------|------|------|-------|------|
| Cement 1    | 23.14 | 4.65  | 3.05  | 64.80| 2.12 | 1.96 | 1.02 | 0.22  | 1.7  |
| Cement 2    | 19.99 | 5.53  | 3.09  | 62.06| 2.68 | 2.42 | 1.03 | 0.38  | 2.5  |
| Cement 3    | 21.63 | 6.28  | 3.66  | 62.01| 2.28 | 2.20 | 0.98 | 0.25  | 1.9  |
| Cement 4    | 20.96 | 5.46  | 3.72  | 61.52| 3.53 | 1.96 | 0.78 | 0.65  | 2.0  |
| Cement 5    | 21.92 | 4.48  | 3.55  | 61.07| 1.96 | 3.99 | 0.79 | 0.55  | 1.9  |

2.2. Synthesis of SP samples
Three self-synthesized SP samples were synthesized by acrylic acid and C5 or C6 macromonomer, which were named as SPV1, SPV2 and SPT1 respectively. Here, the reactions were initiated with redox system while MAC was added as chain transfer agent based on the copolymerization of acrylic acid and macromolecules. In the following, each synthesis method is described in detail.

2.2.1. Synthesis of SPV1
According to this synthesis method, the macromonomer and hydrogen peroxide were placed in the reaction vessel while acrylic acid (solution I), the chain transfer agent and reducing agent (solution II) were separately fed into the reactor in 40min-60 min. The synthesis of SPV1 is taken as an example below:

68.4g VPEG was dissolved in 50mL of deionized water and poured into a 500mL three-neck round-bottom flask. The batch was controlled 8 ℃ by low temperature constant temperature bath. Then, 0.8g hydrogen peroxide was added into the reaction vessel. The solution I was composed of 6.6 g acrylic acid and 20.0 g water, and solution II was composed of 0.1g reducing agent (E51), 0.3 g mercaptopropionic acid (MAC) and 20.0 g deionized water. Both the solutions were simultaneously pumped dropwise onto the reaction mixture. The time of the solution I added was about 40-50min, and the time of the solution II added was about 50-60min. The reaction mixtures were stirred for further 40-50min after all solutions were added completely. At last, 22.9 g deionized water was poured the solution, and SPV1 solution with a solid content of 40wt% was obtained.
2.2.2. Synthesis of SPV2
The same synthesis method was used for SPV1 while the temperature was controlled 35 °C.

2.2.3. Synthesis of SPT1
72.4 g TPEG and 60.0 g water were placed in a 500 mL three-neck round bottomed flask. The temperature was set to 45 °C. After the macromonomer was completely dissolved, 1.0 g hydrogen peroxide was added into the reaction system. Then, 8.7 g acrylic acid was dissolved in the 22 mL deionized water, which named solution I. And solution II was composed of 0.12 g reducing agent (vitamin C), 0.3 g mercaptopropionic acid (MAC) and 32.0 mL deionized water. The solutions (I and II) were simultaneously pumped dropwise onto the reaction vessel. The time of solution I dropped was 150 min and the time of solution II dropped was 180 min. When the solutions were completed, the mixture was curing for another 90 min to finalized the reaction. After that, another 7.4 mL deionized water was poured into the reaction mixture. At last, the SPT1 solution with a solid content of 40wt% was obtained.

2.3. GPC test
Molar masses (Mw, Mn), polydispersity index (PDI) and of the SP samples were tested by gel permeation Chromatography (GPC). The eluent was 0.1 mol/L aqueous NaNO3 and flow rate was 0.5 mL/min.

2.4. Performance test

2.4.1. Cement paste fluidity
Cement paste fluidity was tested based on GB/T 8077-2012 “Method for testing uniformity of concrete admixture”.

2.4.2. Concrete test
Slump and slump lost tests of the concrete refer to GB/T 50080-2016 “Standard for test method of performance on ordinary fresh concrete” and compressive strength is according to GB/T 50081-2019 “Standard for test methods of concrete physical and mechanical properties”. J-ring test refer to JGJ/T 283-2012 “Technical specification of self-compacting concrete”, T500 and V-funnel test are according to CECS203-2006 “Technical specifications for self-compacting concrete application”. The above standards are the current standards in China. The compounding ratio of self-compacting concrete is shown in Table 2, which the composition of the admixture used is shown in Table 3.

| Strength grade | C  | FA | SI | G(5mm-20mm) | S  | W  | admixtures |
|---------------|----|----|----|-------------|----|----|------------|
| C55           | 280| 170| 50 | 854         | 818| 168| 4.2        |

| Sample name   | SPV1 | SPV2 | SPT1 | SP concentration (wt%) | BT | B2 | PN | W |
|---------------|------|------|------|------------------------|----|----|----|---|
| PC-1          | 360  |      |      | 36.0                   | 100| 10 | 30 | 500|
| PC-2          | 385  |      |      | 38.5                   | 100| 10 | 30 | 475|
| PC-3          | 370  |      |      | 37.0                   | 100| 10 | 30 | 490|

Note: BT, B2 and PN stand for slump retaining agent, viscosity modifier and retarder respectively
3. Test Results and Discussions

3.1. Characterization of PCE

The Chemical structures of SPV1, SPV2 and SPT1 is shown in Fig. 1. As can be seen that the side chains of SPV molecule are softer than SPT, and the steric hindrance is lower than SPT. The microscopic properties of the synthesized polymers are shown in Table 4. According to SEC data, the molar mass (Mw) of PCE samples ranged from 35,000 to 11,000 Da. The polydispersity index of the samples ranged from 1.49 to 1.80. Moreover, yields >85% were found, and the yield of SPV1 is significantly higher than SPV2. Thus, low temperature is more beneficial to VPEG synthesis than high temperature. The SEC spectrum of the three PCE are shown in Fig. 2. The main peak of the copolymerized product and the residual peak of the large monomer can be observed.

![Chemical structures of SPV1, SPV2 and SPT1. (a: SPV1 and SPV2, b: SPT1)](image)

![Fig.1 Chemical structures of SPV1, SPV2 and SPT1. (a: SPV1 and SPV2, b: SPT1)](image)

Table 4 Molar masses (Mw, Mn), polydispersity index (PDI) and conversion for the synthesized superplasticizer samples

| Polymer | Mw (g/mol) | Mn (g/mol) | PDI (Mw/Mn) | Conversion of monomers |
|---------|------------|------------|-------------|------------------------|
| SPV1    | 37564      | 24696      | 1.52        | 97%                    |
| SPV2    | 35938      | 24069      | 1.49        | 96%                    |
| SPT1    | 50859      | 28313      | 1.80        | 89%                    |
3.2. Effect of PCEs on cement fluidity

Fig. 2 SEC spectra of SPV1, SPV2 and SPT1.
Fig. 3 Fluidity loss behavior of different cement slurries (w/c=0.29) containing SPV1, SPV2 and SPT1.

(a: C1, b: C2, c: C3, d: C4, e: C5)
The time loss behavior of SPV1, SPV2 and SPT1 in 2 hours was measured. In this test, 5 pCE treated cement slurries as shown in Figure 3 were used, with a W/C ratio of 0.29. According to this data, for all cement, SPV1 retain fluidity of the cement paste considerably better than SPV2 and SPT1. Fig.4 shows Initial fluidity for different cement slurries (w/c=0.29) with SPV1, SPV2 and SPT1. As we can see that for all cement, the initial fluidity of the cement paste with SPT1 are less than SPV1. However, they still perform considerably better than SPV2. Due to the higher Q-e values and polarity of the C6 based macromonomers, free radical copolymerisation with AA generated PCEs with a higher degree of order in the distribution of PEO side chains along the main chain backbone. The orderness became more dominant when the temperature of synthesis was suitably controlled. Thus, SPV1 showed better cement dispersing ability compared to SPT1. In addition, with the change of cement, the initial fluidity of cement paste containing SPV1 are less sensitive than SPT1 and SPV2. This is due to that SPV side chain is softer than SPT, which improves the enveloping and winding property of polyether side chain, showing better adaptability to cement. Besides, as Table 5 shows, the yield of SPV2 is significantly lower than SPV1 and SPT1, the initial fluidity of cement paste mixing with SPV2 is the minimum.

| Sample | Initial Slump flow (mm) | V-funnel flow time (s) | T500 (s) | J-ring blocking step (mm) | Air content (%) | Compressive strength (MPa) |
|--------|-------------------------|------------------------|----------|--------------------------|----------------|--------------------------|
| SPV1   | 690                     | 13                     | 12       | 4                        | 3.2            | 66.7                     |
| SPV2   | 675                     | 18                     | 11       | 10                       | 3.1            | 65.3                     |
| SPT1   | 680                     | 20                     | 9        | 8                        | 3.3            | 66.5                     |
Fig. 5 Slump loss behavior of SCC containing SPV1, SPV2 and SPT1.

The results of various fresh properties tested by slump flow test (slump flow diameter and T500 mm), J-ring test (J-ring blocking step (BJ); V-funnel test; air content test are given in Table 5. In the table the compressive strength results are also recorded.

Fig. 5 gives the slump loss behavior of SCC containing SPV1, SPV2 and SPT1 and initial flow slumps are showed in Table 5. While the flow slump of concrete is control at 680±10mm, the concentration of SP in admixture from high to low are SPV2, SPT1 and SPV1. SPV1 retain fluidity of the concrete considerably better than SPV2 and SPT1. These indicate that the dispersing ability and retention ability of SPV1 on concrete is more superior than SPV2 and SPT1. This is also consistent with the result of 3.2.

T500 is mainly used to characterize the viscosity and flow rate of concrete. From table 4, we can see that the T500 mm slump flow for these three SPs are different, the flow time for SPV1 and SPV2 are longer than SPT1. It means that plastic viscosity of cement with SPT1 is lower than SPV1 and SPV2, that suggesting that TPEG-PCEs are more benefit than VPEG-PCEs on viscosity of cement. It may be because that SPV side chain is softer than SPT, which improves the enveloping and winding property of polyether side chain, and retards some free motion, thus increase the plastic viscosity of mortar.

V-funnel test is used to measure the viscosity and segregation resistance of self-compacting concrete. In table 5, obvious differences in the speed of flow were observed for three kinds of PCEs. The longest times to empty were found for SPT1 (20s), superior performance is observed from concrete prepared with SPV2, its time to empty is shorter, and the best is SPV2, 13s only, which is contrary to T500 mm slump flow. It shows that workability of concrete can be improved by cohesion increasing.

The J-ring method is mainly used to test the ability of self-compacting concrete to pass through steel bars in plane. If the value of blocking step is closer to zero, it indicates better filling and passing ability. the blocking steps from low to high are SPV2, SPT1 and SPV1, which is in accord with V-funnel flow time.

Besides, the air content and compressive strength of concrete does not change significantly with different PCEs.
4. Conclusion
Based on the experimental results, following conclusions can be drawn that low temperature is more beneficial to VPEG synthesis than high temperature. As VPEG-PCEs side chain is softer than TPEG-PCEs, which improves the enveloping and winding property of polyether side chain, showing better adaptability to cement. Besides, Initial fluidity and retain fluidity of the cement paste with VPEG-PCEs also considerably better than TPEG-PCEs. SCC with TPEG-PCEs shows lower viscosity than SCC with VPEG-PCEs. However, the flow ability and passing ability of SCC increased adding with VPEG-PCEs compared to TPEG-PCEs.

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