

# Synthesis and Application of a New Vinyl Copolymer Superplasticizer

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**ABSTRACT:** A new vinyl graft copolymer superplasticizer was synthesized by copolymerization of polyethylene glycol acrylate (PEGAA), polyethylene glycol biester of maleic acid and citric acid (PEGMC), acrylic acid (AA), sodium allylsulphonate (SAS), and methyl acrylate (MA). The effects of the vinyl monomers' molar ratio, initiator, reaction temperature, and reaction time on its application properties were investigated. The results show that the new vinyl graft copolymer superplasticizer has excellent application properties when the molar ratio of PEGAA, PEGMC, AA, SAS, and MA is 0.5 : 0.10 : 0.20 : 0.05 : 0.03 and the initiator ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, APS] is 0.8 wt % at 80°C for 3 h. The vinyl

monomers' conversion is 98.7%. The applied results show that the water-reducing ratio and retardation solidification time of the superplasticizer reach 33.5% and 4 h, respectively. The applied concrete has excellent mechanical properties. Its molecular structure was characterized by nuclear magnetic resonance, Fourier transform infrared spectra, and gel permeation chromatography. It is characteristic of the new vinyl graft copolymer superplasticizer that citric acid (CA) and MA are introduced into the copolymer molecules. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 273–280, 2010

**Key words:** synthesis; copolymerization; graft copolymers

## INTRODUCTION

The functions of superplasticizer or water-reducing agent added to concrete can not only remarkably improve workability of concrete, but also make a large increase in mechanical properties of concrete construction. Consequently, the superplasticizer has been broadly applied in concrete construction at present, and it has played a significant role in concrete engineering because, it was found and synthesized easily.<sup>1–4</sup> The vinyl polymer superplasticizer was first synthesized by Japanese scientist in the 1980s. Because of its high water-reducing ratio and excellent mechanical properties, it was called the third generation high-performance superplasticizer after ligno-sulfate based plasticizer and naphthalene-sulfonate (NPS) based plasticizer.<sup>5–9</sup> Except for high wafer-reducing ratio and high strength, the vinyl copolymer superplasticizer also has other advantages, for example, it is required in lower dosage and it is nonpollutant to environment. Therefore, the

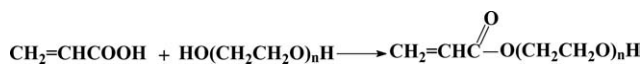
vinyl copolymer superplasticizer has gained considerable importance in recent years.<sup>10–13</sup> Unfortunately, the vinyl copolymer superplasticizer has also some disadvantages in application, for example, it is easy to separate or isolate water from concrete, and it is not compatible with retarder. These disadvantages restrict and limit its further application.

In this article, a new vinyl graft copolymer superplasticizer was synthesized by copolymerization of polyethylene glycol acrylate (PEGAA), polyethylene glycol biester of maleic acid and citric acid (PEGMC), acrylic acid (AA), sodium allylsulphonate (SAS), and methyl acrylate (MA). It was a characteristic feature of the new vinyl graft copolymer superplasticizer that PEGMC and MA are used as monomers and citric acid (CA) was grafted onto the copolymer molecule, which makes it different from conventional vinyl copolymer superplasticizers in structure and applied properties. The motive of the synthesis is to gain good application properties, improve resistance, isolate water, and improve its compatibility with other composition. During the last decade, various vinyl copolymer superplasticizers were synthesized and reported by many references. But all the monomers used for synthesis were restricted including PEGAA, SAS, methacrylic acid, and AA.<sup>14,15</sup> The goal of introducing CA and MA into the copolymer molecule is to produce coordination effect among the functional groups and adjust the properties so that it can bring good applied

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**Figure 1** The schematic diagram of synthesis of PEGAA by AA and PEG.

results. The applied results show that the new vinyl graft copolymer superplasticizer is superior to conventional vinyl copolymer products in resistance, isolate water, and compatible with other composition. In synthesis experiment, the effects of the molar ratio of monomers, concentration of initiator, reaction temperature, and reaction time on applied properties were investigated. The structure of the new graft copolymer superplasticizer was characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectra, and gel permeation chromatography (GPC).

## EXPERIMENTAL

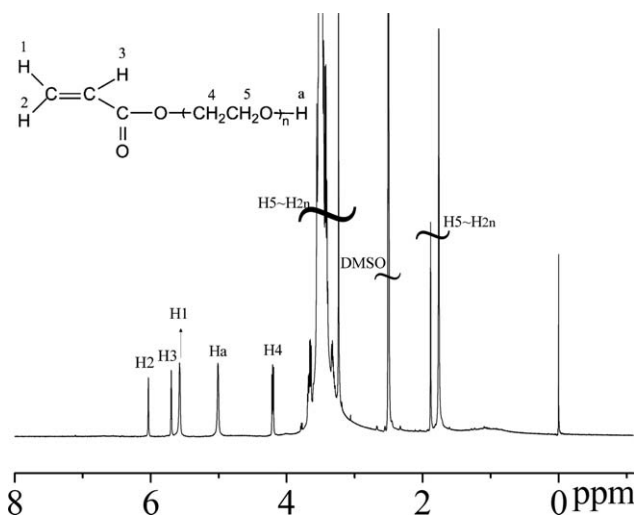
### Materials

Polyethylene glycol (PEG) 400–1200, citric acid (CA), maleic anhydride (MAH), methyl acrylate (MA), acrylic acid (AA), sodium allylsulphonate (SAS), *p*-toluenesulfonic acid (PTSA), ammonium persulfate ( $(\text{NH}_4)_2\text{SO}_4$  (APS), hydroquinone, and sodium hydroxide (NaOH) were chemical grade and purchased from Xi'an chemical reagent factory (China). Other chemicals were reagent grade and bought from Xi'an chemical reagent factory (China). Cements, including Qinling 42.5R, Shengwei 42.5R, and Jidong 42.5R were supplied by Shaanxi Cement (China). The standard cement was supplied by Beijing Xingfa Cement (China).

### Synthesis of the polyethylene glycol acrylate

The equimolar of PEG (800–1200) and AA were taken in a 500 mL three-neck round-bottom flask with a stirrer and an intelligent control temperature device. By stirring, the temperature was slowly raised to 60°C, and then 1 wt % PTSA (relative to the mass of PEG) and 1 wt % hydroquinone (relative to the mass of AA) were added together into the flask. The temperature was raised to 85–90°C, maintained for 2 h, and then cooled to ambient temperature. The product is the PEGAA. The specimens used for the test were further purified by repeated precipitation with acetone-methanol mix solvent. The schematic diagram of the synthesis of PEGAA by AA and PEG is shown in Figure 1. The chemical structure of PEGAA was verified by NMR and FTIR, and the results are shown in Figure 2, Figure 3, and Figure 7. The data are analyzed as follows.

$^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ,  $\delta$ , ppm): 6.034 (H2), 5.575 (H1), 5.700 (H3), 5.696 (H3), 5.692 (H3), 5.010



**Figure 2** The  $^1\text{H-NMR}$  of PEGAA.

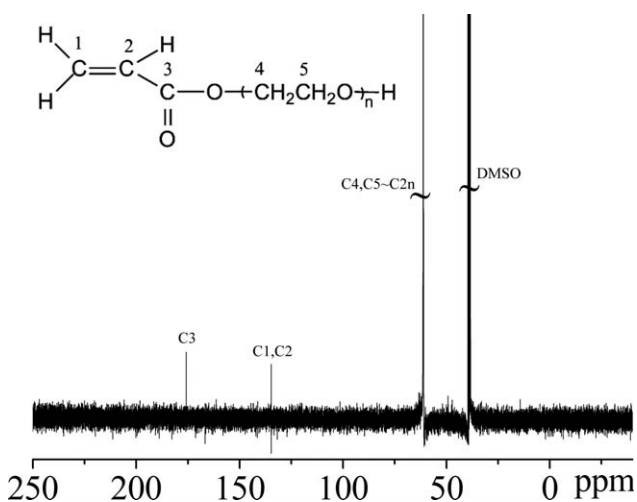
(Ha), 4.217 (H4), 4.205 (H4), 4.201 (H4), 3.557 (H5), 3.539 (H5), 3.507 (H5), 3.470 (H5), 3.238 (H5), 1.883 (H5), 1.763 (H5).

$^{13}\text{C-NMR}$  (125 MHz,  $\text{DMSO-}d_6$ ,  $\delta$ , ppm): 175.781 (C3), 134.715 (C1, C2), 61.456, 61.372, 61.353, 61.262, 61.180, 61.096 (C4, C5).

FTIR (KBr, thin coating,  $\text{cm}^{-1}$ ): 3400 (OH), 1740 (COOC), 1609 (C=C), 1200, 1186 ( $\text{CH}_2\text{OCH}_2$ ).

### Synthesis of the polyethylene glycol biester of maleic acid and citric acid

The equimolar of PEG-400 and MAH were taken in a flask as above. Then the reactant was heated up to 90°C and the temperature was maintained for 2 h. Equimolar of CA (relative to mole of PEG) was added to the flask. The temperature was raised to 100°C and maintained for 2 h. Then, by cooling to



**Figure 3** The  $^{13}\text{C-NMR}$  of PEGAA.

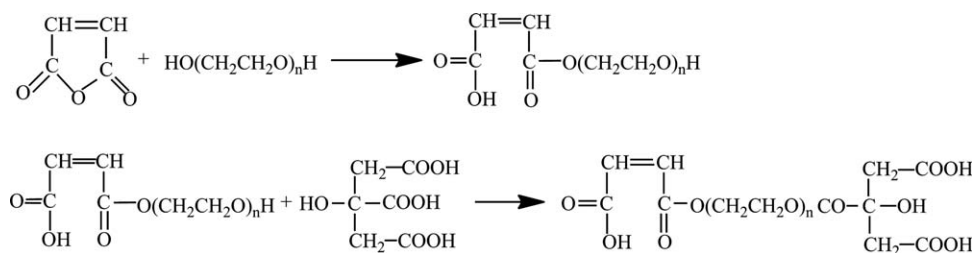


Figure 4 The schematic diagram of synthesis of PEGMC by maleic acid and citric acid.

ambient temperature, PEGMC was obtained. The specimens used for the test were further purified. The synthesis reaction of the PEGMC is shown in Figure 4. The PEGMC was tested by NMR and FTIR. The test results are shown in Figure 5, Figure 6, and Figure 7. The data are analyzed as follows.

<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD, δ, ppm): 9.951 (H1), 9.122 (H5), 9.101 (H8), 6.600 (H2), 6.324 (H3), 4.712–5.096 (H9, H10), 3.779 (H6), 2.613 (H4, H7).

<sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 175.773 (C7, C10), 166.695 (C1, C4, C5), 134.727 (C2), 109.901 (C3), 62.841 (C8), 61.177, 61.751, 62.289 (C11, C11–C2n), 39.036 (C6, C9).

FT-IR (KBr, thin coating, cm<sup>-1</sup>): 3300 (OH), 1730 (COOH), 1609 (C=C), 1200, 1193 (CH<sub>2</sub>OCH<sub>2</sub>).

### Synthesis of the vinyl graft copolymer superplasticizer

Certain amount of distilled water was added to the flask as above and heated. When its temperature was about 80°C, the vinyl monomers mixture and the initiator solution were added dropwise to the flask at the same time. The monomers mixture include PEGAA, PEGMC, MA, AA, and SAS, and the molar ratio of PEGAA, AA, SAS, and MA is 0.5 : 0.20 : 0.05 : 0.03, and the molar ratio of PEGMC rela-

tive to other monomers is shown in Table I. The mass fraction concentration of all monomers was controlled at about 20 wt %. The initiator solution was obtained by dissolving 0.8 wt % APS (relative to the total mass of the vinyl monomers mixture) in distilled water. The vinyl monomers mixture and the initiator solution were added dropwise to the flask within 50–60 min. The copolymerization was carried out at 80°C for 3 h. Then the product was cooled to room temperature and neutralized to pH 8.0 with 20 wt % NaOH solution. The product was the new superplasticizer. Its structure was approved by FTIR. The result is shown in Figure 7. FTIR (KBr, thin coating, cm<sup>-1</sup>): 3500 (OH), 1758 (COO), 1409, 1353 (SO<sub>3</sub><sup>-</sup>) 1200, 1193 (CH<sub>2</sub>OCH<sub>2</sub>). The schematic diagram of synthesis of the new vinyl graft copolymer superplasticizer is shown in Figure 8.

### Tests and measurements

The vinyl monomers conversion was determined according to the People's Republic of China National Standard methods (GB/T 601-2002 and GB 1676-81).

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were tested on an INOVA-400MHz spectrometer (Varian, Palo Alto, USA). Samples for <sup>1</sup>H-NMR were prepared in deuterated methanol (CD<sub>3</sub>OD), and samples for <sup>13</sup>C-

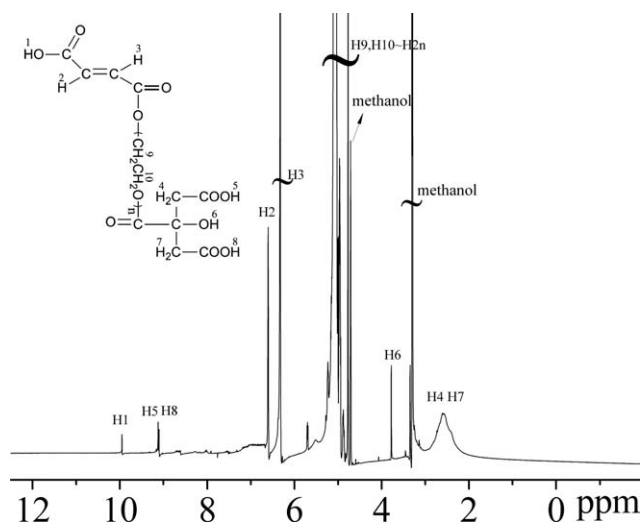


Figure 5 The <sup>1</sup>H-NMR of PEGMC.

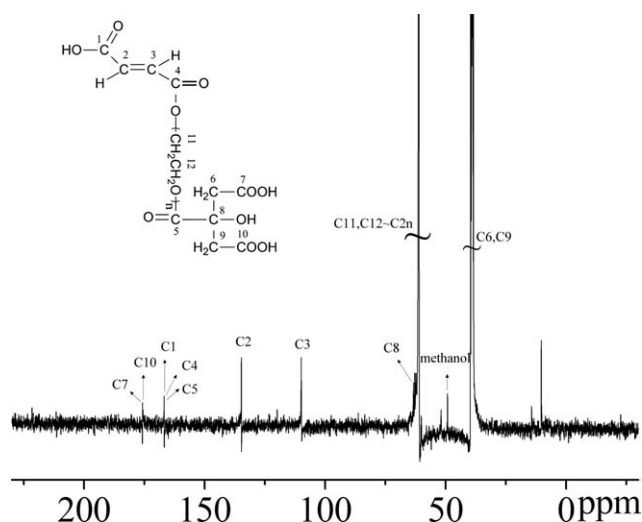
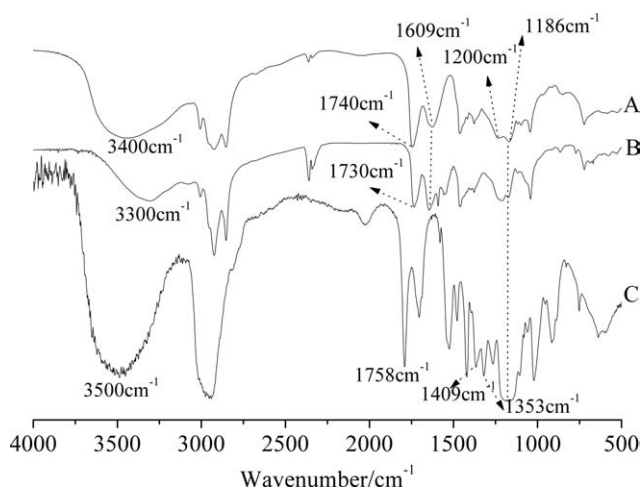


Figure 6 The <sup>13</sup>C-NMR of PEGMC.



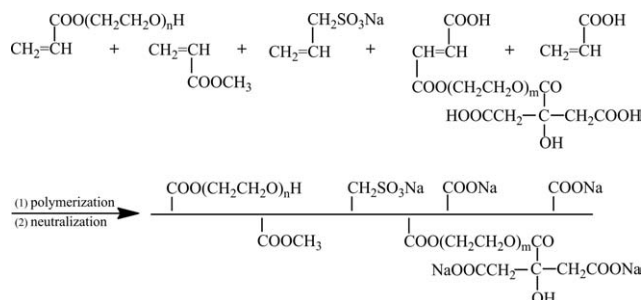
**Figure 7** The FTIR of PEGAA (A), PEGMC (B), and the new vinyl graft copolymer superplasticizer (C).

NMR were prepared in deuterated dimethyl sulfoxide (DMSO- $d_6$ ).

The FTIR was verified by FTIR Spectrometer of VECTOR 22, made by German BRUKER Company (Kleve, Germany). The copolymer was purified via dissolution and precipitation for at least three times. Then the product was dried in vacuum at 60°C for 24 h.

The relative molecular weight and polydispersity index were characterized by GPC of model 2414, made by American Waters Instruments Co. Ltd. (Milford, MA). Two columns set (Ultrahydrogel 250 and 120, 7.8 × 300 mm, Waters) were used in series. The mobile phase consisted of a solution of 0.10 mol/L sodium nitrate, its flow rate was 0.42 mL/min, test temperature was 50°C, and the standard sample was polyethylene glycol.

The surface tension of the new graft copolymer superplasticizer solution was determined by an automatic surface tension apparatus of JK99B. The solution was obtained by dissolving the superplasticizer in distilled water so that its mass concentration



**Figure 8** The schematic diagram of synthesis of the new vinyl graft copolymer superplasticizer.

was 1 wt %. The cement particles zeta-potential were determined by a microscopic-electrophoresis instrument of JS94H. The JK99B and JS94H were produced by Shanghai Zhongchen Digit Technic Instrument Co. Ltd., China. The specimen was prepared by adding vinyl graft copolymer superplasticizer 0.25 g and cement 1 g to 100 mL distilled water in volumetric flask together. The samples were examined for 5 times.

The applied properties of the graft copolymer superplasticizer were determined according to the People's Republic of China National Standard Methods (GB/T8077-2000).

## RESULTS AND DISCUSSIONS

### Effects of MA content on the fluidity and the slump-loss

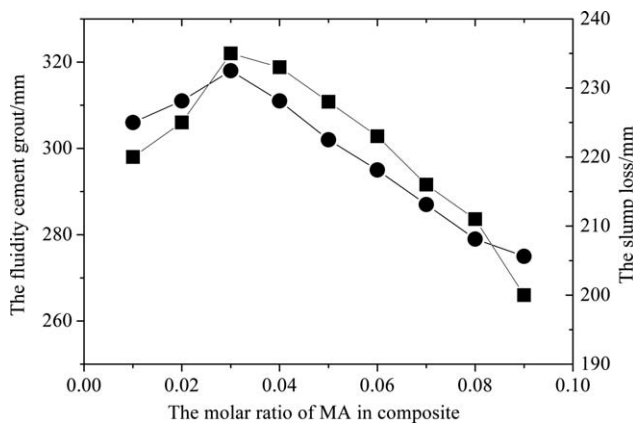
The influences of MA content in the monomers on the fluidity of cement grout and the slump-loss of concrete are shown in Figure 9. It is observed from the figure that the fluidity of cement grout and the slump-loss increase rapidly with increasing MA content until 0.03M ratio, and then slightly decrease with further increasing in MA content. It is beneficial to improve the surface activity of the vinyl graft

**TABLE I**  
The Effects of PEGMC Content on Properties of the New Superplasticizer

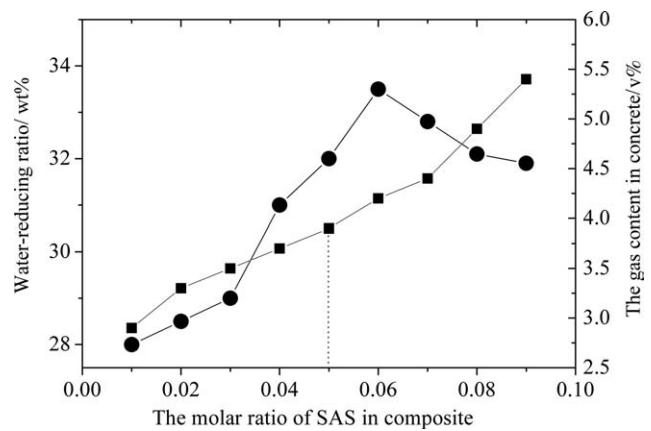
PEGMC <sup>a</sup> (mole)	Water-reducing ratio (wt %)	The water separated from concrete (wt %)	Slump-loss <sup>b</sup> (mm)				Compression strength specific <sup>a,b</sup> (%)		
			0 min	60 min	180 min	360 min	3d	7d	28d
0.050	30	15	248	187	144	112	201	175	151
0.075	31	8	245	218	175	115	197	168	150
0.100	34	3	242	240	230	225	198	172	156
0.125	27	2	245	189	176	145	185	145	140
0.150	24	1	226	179	168	136	164	139	135
0.200	20	0	218	168	161	129	152	124	122

<sup>a</sup> Composite concrete included cement (standard cement) 2.52 kg, coal ash 1.08 kg, sand 7.61 kg, bag cobble 2.11 kg, middle cobble 5.25 kg, small cobble 3.15 kg, and water 1.48 kg.

<sup>b</sup> The new vinyl graft copolymer superplasticizer's dosage is 0.2 wt % according to solid superplasticizer mass. The superplasticizer dosage 0.2 wt % is added to concrete according to solid cement mass.



**Figure 9** The effects of MA content on the cement grout fluidity (●) and the slump-loss (■) [The molar ratio of *n* (PEGAA): *n* (PEGMC): *n* (AA): *n* (SAS) is 0.5 : 0.10 : 0.20 : 0.05. The cement is standard cement Xingfa].



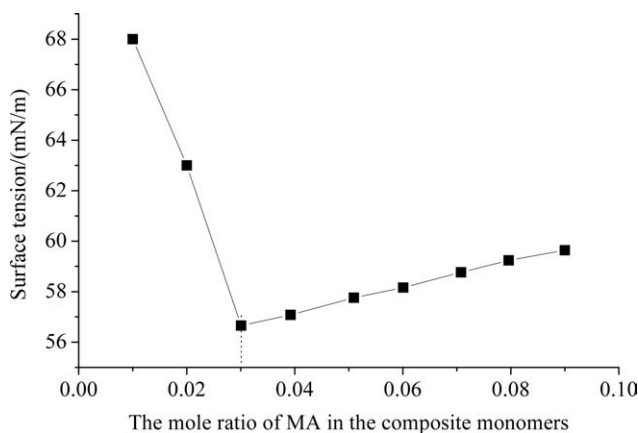
**Figure 11** The effects of SAS content on water-reducing ratio (●) and the gas content (■) [The molar ratio of *n* (PEGAA): *n* (PEGMC): *n* (AA): *n* (MA) is 0.5 : 0.10 : 0.20 : 0.03. The cement was standard cement Xingfa].

copolymer superplasticizer by introducing MA into copolymer molecule. Therefore, it can increase fluidity of cement grout and decrease slump-loss of concrete. The conclusion is supported by the surface tension decreasing with the increase of MA content, and its surface tension is shown in Figure 10. When the sample concentration is 0.03 mol in copolymer, the surface tension of the copolymer solution reaches the minimum. Therefore, the optimum MA content is 0.03M ratio in the composite monomers.

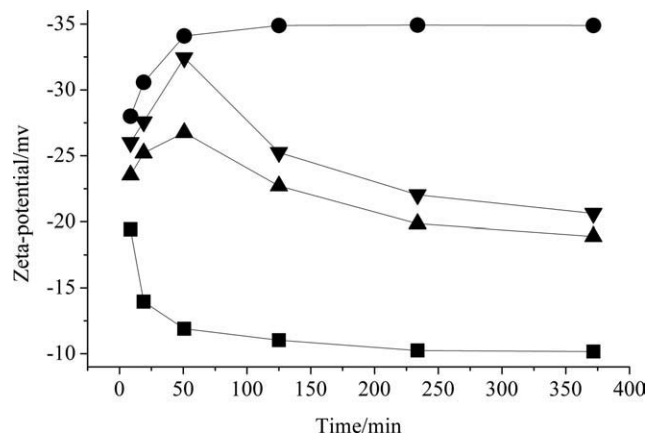
**Effects of SAS content on the water-reducing ratio and the gas content**

Figure 11 shows the effect of SAS content in the monomers on the water-reducing ratio and the gas content of concrete. The function of SAS in the copolymer is to produce gas in applied concrete. It can be seen from the Figure 11 that, with the increase of SAS content, both water-reducing ratio and the gas

content increase quickly. The water-reducing ratio increases with increasing SAS content until 0.05M ratio and then decrease slightly. The maximum water-reducing ratio is 33.5% and occurred at 0.06M ratio (SAS content). The appropriate gas content in concrete is beneficial as it improves the concrete fluidity, and hence can be transferred by pipe easily for construction. But the gas in the concrete decreases the mechanical strengths, because gas in the concrete cannot make the concrete becomes dense during construction. The gas content should be less than 4.0 v % according to the People’s Republic of China National Standard GB/T8077-2000. Consequently, the optimum SAS content is 0.05M ratio in the monomers.



**Figure 10** The effects of MA content on the surface tension of the superplasticizer solution. (The monomers composition are the same as Fig. 2).



**Figure 12** The effect of PEGMC on the cement  $\zeta$ -potential (●: the solution is added the new vinyl graft copolymer superplasticizer; ▼: the solution is added the mixture of citric acid (2.0 wt %) and the conventional vinyl copolymer superplasticizer; ▲: the solution is only added the conventional vinyl copolymer superplasticizer; ■: the solution is only constituted by water and cement. The cement was standard cement Xingfa).

**TABLE II**  
The Relative Molecular Weight of the New Superplasticizer

Superplasticizer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_p$	Polydispersity index	Water-reducing ratio <sup>a</sup> (wt %)
The new superplasticizer	2319	4573	4526	1.95	34.5
FOX <sup>b</sup>	2567	3658	4421	1.43	29.8
KDPCA <sup>c</sup>	1856	2654	3965	1.42	31.2
vinyl graft copolymer (1) <sup>d</sup>	5604	43057	61882	7.68	19.8
vinyl graft copolymer (2) <sup>d</sup>	963	3993	2261	4.15	9.7

<sup>a</sup> The solid dosage of the superplasticizer is 0.2 wt % relative to cement mass.

<sup>b</sup> FOX is a vinyl copolymer superplasticizer produced by Chinese Fuclear Chemical Science and Technology. Its major functional groups are  $-\text{COOH}$  and  $-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$ .

<sup>c</sup> KDPCA is a vinyl graft copolymer superplasticizer supplied by Beijing XinJunJie construction materials factory and produced by Japan. Its major functional groups are  $-\text{COONa}$ ,  $-\text{SO}_3\text{Na}$ , and  $-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$ .

<sup>d</sup> The monomers of two vinyl graft copolymer are same with the new vinyl graft copolymer superplasticizer. They have only difference in the molecular weight.

### Effects of PEGMC content on the superplasticizer properties

The effects of PEGMC content in superplasticizer on the applied properties are shown in Table I. The results show that vinyl graft copolymer superplasticizer, into which PEGMC is introduced, has an advantage of extending set-retarding time and resistance isolated water. The retardation solidification time increases with PEGMC content until 0.100 mol and then decrease slightly. The weakness of separating water and cement from concrete become almost disappears when PEGMC content increases. The maximum specific compressible strength of concrete occurred at 0.100 mol of PEGMC content. According to the above facts, the conclusion is that there is stronger force among functional groups of CA,  $-\text{COOCH}_3$ ,  $-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$ , and cement particle. Consequently, the new graft copolymer superplasticizer could gain excellent properties such as high water-reducing ratio and retardation solidification time. Especially, resistance isolate water and compatible capability is superior markedly to conventional vinyl copolymer products.

In conclusion, the new graft copolymer superplasticizer is synthesized by copolymerization at 80°C for 3 h when molar ratio of PEGAA, PEGMC, AA, SAS, and MA is 0.5 : 0.10 : 0.20 :

0.05 : 0.03 and the initiator APS is 0.8 wt %. The monomers conversion is 98.7%.

### Effect of PEGMC on the cement particle $\zeta$ -potential

The solution is prepared with cement and water. The cement particle zeta-potential in the solution is shown in Figure 12. It is found from the results that the cement particle zeta-potential decrease rapidly within initial 60 min without additives in the solution. When the conventional vinyl copolymer superplasticizer (copolymer molecule without PEGMC) is added to the solution, the cement particle zeta-potential increases in initial 50 min and then slightly decreases. When the mixture of CA and the conventional vinyl copolymer superplasticizer are added to the solution, the cement particle zeta-potential increase remarkably in initial 50 min and then decrease slightly. When the new graft copolymer superplasticizer is added to the solution, the cement zeta-potential increase rapidly with the time for 60 min and then level off, and the cement particle zeta-potential value is also the highest in the four solutions. This fact explain that the new vinyl graft copolymer introduced the PEGMC not only improve the interaction between superplasticizer molecule and the cement particle but also produce a coordination effect among all functional groups.

**TABLE III**  
The Chemical and Physical Properties Test Results of the New Vinyl Graft Copolymer Superplasticizer

Test items	appearance	Solid content (wt %)	Density (g/cm <sup>3</sup> )	pH	Cl <sup>-</sup> content (wt %)	Surface tension (mN/m)	Base content (wt %)	Formaldehyde content (wt %)
Determined value	Light purple liquid	20.7	1.063	7.0	0	56.5	1.3	0

**TABLE IV**  
The Applied Results of the New Superplasticizer

Items	The new superplasticizer	FOX <sup>a</sup>	KDPCA <sup>a</sup>	NPS <sup>a</sup>
Added content (relative to cement) (wt %)	0.20	0.20	0.20	0.75
Water-reducing ratio (wt %)	34.5	29.8	31.2	13.8
Gas content (v %)	2.8	4.4	5.1	1.3
Separated water from concrete (wt %)	1.6	4.0	2.5	12
The coagulated start time (min)	94	100	102	15
The coagulated end time (min)	103	198	116	10

<sup>a</sup> NPS is naphthalene-sulphonate plasticizer, and FOX and KDPCA are the same as Table II. The cement is standard cement Xingfa.

Consequently, the cement particle zeta-potential can be kept stable for 6 h.

### The molecular weight of the vinyl graft copolymer superplasticizer

The molecular weight of the new vinyl graft copolymer superplasticizer is shown in Table II. The number-average molecular weight of the new vinyl graft copolymer superplasticizer is 2319, mass-average molecular weight is 4573, the peak molecular weight is 4526, and the polydispersity index is 1.95. These results indicate that the polydispersity of the vinyl graft copolymer superplasticizer is the largest among the three specimens. The results also show that the control of the molecule weight of vinyl copolymer superplasticizer is very important in synthesis of vinyl copolymer superplasticizer.

### The applied results of the new vinyl graft copolymer superplasticizer

The chemical and the physical properties test results of the new vinyl graft copolymer superplasticizer are shown in Table III. The test results exhibit that all chemical and physical index corre-

spond with National Standard Methods GB/T8077-2000. Especially, the superplasticizer has no chloride ions and formaldehyde, so it has corrosion resistance on iron in the concrete and would not produce pollution to environment in contrast to plasticizer based on NPS.

The applied results of the new vinyl copolymer superplasticizer are shown in Table IV. The results show that the new vinyl copolymer superplasticizer has the following features: required in small dosage, has a high water-reducing rate, and has an excellent performance, such as good dispersibility, better flow-keeping ability, excellent compatibility, and higher strength.

The applied results of the new vinyl graft copolymer superplasticizer in the concrete are shown in Table V. The results indicate that the new vinyl graft copolymer superplasticizer has many advantages, such as good compatibility with various cements, superior workability, and higher compressive strength. Hence, this new vinyl graft copolymer superplasticizer should have an excellent applied performance.

## CONCLUSIONS

A new vinyl graft copolymer superplasticizer was synthesized by copolymerization of PEGAA,

**TABLE V**  
The Applied Results of the New Superplasticizer in Concrete

Cement	Superplasticizer	Dosage (wt %)	Water (kg)	Water-reducing ratio (wt %)	The slump-loss <sup>a</sup> (mm)				Compression strength (MPa)		
					0 min	30 min	60 min	300 min	3d	7d	28d
Qinling 42.5R <sup>b</sup>	NPS <sup>c</sup>	0.90	178	14.3	225	180	120	–	37.2	44.2	53.6
	FOX <sup>d</sup>	0.25	178	28.7	220	195	149	56	39.8	48.2	59.8
	KDPCA <sup>d</sup>	0.25	178	31.6	240	225	220	145	42.5	48.5	57.6
	The superplasticizer	0.25	178	33.4	245	240	245	231	45.8	51.6	62.8
Shengwei 42.5R <sup>b</sup>	The superplasticizer	0.25	178	34.3	256	255	253	247	46.7	55.3	64.1
Jidong 42.5R <sup>b</sup>	The superplasticizer	0.25	178	31.8	249	249	248	237	43.5	50.6	59.4

<sup>a</sup> The concrete are made of cement, sand, cobble, and water according to mass ratio is 330 : 710 : 155 : 210, respectively.

<sup>b</sup> Qinling 42.5R, Shengwei 42.5R, and Jidong 42.5R are three different kinds of cement produced by China.

<sup>c</sup> NPS is naphthalene-sulphonate plasticizer.

<sup>d</sup> FOX and KDPCA are the same as Table II.

PEGMC, AA, SAS, and MA, and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was initiator. The superplasticizer has excellent applied properties when the molar ratio of PEGAA, PEGMC, AA, SAS, and MA was 0.5 : 0.10 : 0.20 : 0.05 : 0.03 and the initiator was 0.8 wt % at 80°C for 3 h. It is characteristic of the new vinyl graft copolymer superplasticizer that CA and MA are introduced into the copolymer molecules. The applied results show that the new vinyl graft copolymer superplasticizer is superior to conventional vinyl copolymer superplasticizer in resistance, in isolating water and in compatible capability.

### References

1. Xia, X. Y.; Xu, Z. X.; Tang, M. S. *Fine Chem* 2004, 21, 17.
2. Ruan, Q. *Guangdong Build Mater* 2004, 5, 1.
3. Agar, W. K.; Masood, I.; Malhotras, K. *Constr Build Mater* 2005, 18, 253.
4. Gong, J.; Guan, X.; Zhang, R. *J Henan Polytechnic Univ (Nat Sci)* 2006, 25, 65.
5. Kreppelt, F.; Weibel, M.; Zampini, D. *Cem Concr Res* 2004, 32, 187.
6. Yamada, K.; Ogawa, S.; Hanehara, S. *Cem Concr Res* 2005, 35, 375.
7. Yamada, K.; Takahashi, T. *Cem Concr Res* 2004, 34, 197.
8. Xi, Q.; Zhu, B. *Mod Chem Ind* 2004, 24, 38.
9. You, C.; Ding, C. *Polym Mater Sci Eng* 2003, 19, 34.
10. Li, C.; Feng, N. *J Build Mater* 2004, 7, 252.
11. Wang, H.; Chen, Z. *Chin J Colloid Polym* 2004, 23, 31.
12. Feng, L.; Wang, X.; Wei, Y. *Cem Concr Prod* 2004, 30, 16.
13. Liu, C. *Chem Mater Constr* 2005, 21, 41.
14. Li, C.; Feng, N. *J Build Mater* 2004, 7, 194.
15. Uchikawa, H.; Sawaki, D.; Hanehara, S. *Cem Concr Res* 1995, 25, 353.