

# Terpolymerization and Performance of 2-acrylamide-2-methyl Propane Sulfonic Acid / Itaconic Acid / *N*-vinyl-2-pyrrolidone

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**ABSTRACT:** Using 2-acrylamide-2-methyl propane sulfonic acid (AMPS), itaconic acid (IA), and *N*-vinyl-2-pyrrolidone (NVP) as monomers, a new retarder terpolymer AMPS/IA/NVP (PAIN) was synthesized by free radical aqueous solution copolymerization and characterized by FTIR and H-NMR. Through the orthogonal experiment, the optimum reaction conditions of copolymerization were obtained: NVP 7.5 wt (mass fraction) %; regulator V 4%; reaction temperature 60°C; initiator 1 wt %. The intrinsic viscosity number of PAIN synthesized with different amount of regulator (isopropanol) was determined, finding that the regulator can change the molecular weight and distribution of PAIN. Through the thickening

experiment in high temperature and high pressure, it was found that PAIN had an excellent retardation property in high temperature, and the thickening times of the cement slurries with 1% (BOWC) PAIN were up to 256 min at 110°C and 234 min at 130°C, respectively. The PAIN was even stable when the temperature below 350°C proved by TG-SDTA analysis. Moreover, the retarding mechanism of PAIN was analyzed and discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2951–2957, 2010

**Key words:** terpolymerization; FTIR; NMR; high-temperature materials; high-performance polymers

## INTRODUCTION

To meet technical requirements of well cementing operation, the retarder are often added into cement slurry to prolong its pumpable time, because the thickening time is the most important parameters in a cement job. In recent years, a number of new retarders have been continuously developed; the two major categories include low molecular organic compounds and polymers. Relatively speaking, the low molecular organic compounds retarder need less dosage, but it is too sensitive; and polymer retarder need larger dosage, but it has a good linear relationship between the dosage and the thickening time, so polymers have become the developmental focuses by virtue of its designable and stable performance since 1990s.<sup>1–6</sup> AMPS have some advantages, such as high activities and excellent temperature and salt resistance, so it is often used as skeleton of copolymers. Several typical products are as follows: AMPS/AA (acrylic acid), AMPS/IA, AMPS/MA (maleic acid), AMPS/IA/AA, and AMPS/IA/AM (acrylamide).<sup>7</sup> Klein and Larry prepared medium temperature retarder with superior performance by

reactions of functional groups.<sup>8</sup> Qi et al. successfully synthesized excellent polymer retarder by copolymerization of AMPS and IA, but it can not be used under high temperature.<sup>9</sup> However, in recent years, the petroleum exploration and development have gradually been emphasized on the deep formation, the ambient temperature of cementing operation has been getting higher and higher, so it is urgent to research and develop a high temperature retarder.<sup>10–12</sup>

In this article, a new retarder terpolymer PAIN was synthesized by terpolymerization of AMPS, IA, and NVP, and it has an excellent retardation property in high temperature by performance test.

## EXPERIMENTAL

### Reagents

AMPS, industrial grade; NVP(99.9%), IA, CA (citric acid), isopropanol, sodium hydroxide, sodium persulfate, and sodium bisulfite, analytical reagent; distilled water.

### Synthesis of PAIN

Some AMPS and IA monomers were added into the prepared sodium hydroxide solution, then a certain amount of NVP was dropped into the beaker filled with this solution was put into ultrasonic cleaner with around 20 s oscillating, thus, fully dispersing

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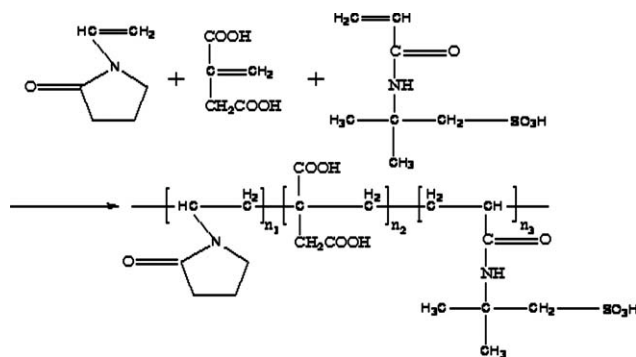


Figure 1 Schematic diagram of copolymerization.

and dissolving. The pH value of the aforementioned solution was adjusted to 8–10 with 0.5 mol/L NaOH, and it was removed into a four neck flask with thermometer, condenser tube, and stirrer, and then heated to reaction temperature, the initiator was dropped into with existing of nitrogen. After a period of time, the regulator was dropped into, reacting 4 h, in constant temperature. So the terpolymer PAIN was obtained, and the reaction equation is shown in Figure 1.

### Purification and analysis of PAIN

The terpolymer was extracted by adding acetone in the liquid system after copolymerization, dried, and pulverized, then dissolved in distilled water. After repeated extraction, drying, grinding of three times, a yellow powder was obtained. NICOLET MX-1E (Nicolet, USA, in the range from 400–4000  $\text{cm}^{-1}$ ) Fourier infrared spectrometer and Avance Bruker 600M NMR Spectrometer (Swiss Bruker Corporation; solvent,  $\text{D}_2\text{O}$ ) were used to confirm the formation of terpolymer PAIN. Mettler Toledo thermogravimetric and differential thermal combined analyzer of type TGA/SDTA851e was used to check out the performance under high temperature. The temperature range was from 50 to 500°C at heating rate of 10°C/min. An ubbelohde viscometer was used to measure intrinsic viscosity number of PAIN with 1 mol/L sodium chloride solution.

### Performance evaluation of the PAIN

The performance of PAIN was evaluated according to Part 1 (retarder) evaluation method for well cement additives (SY/T 5504.1).

## RESULTS AND DISCUSSION

### Reaction condition

According to the mechanism of radical polymerization, the main influencing factors of performances of

TABLE I  
Orthogonal Table of Copolymerization

NO.	A (°C)	B (wt %)	C (wt %)	D (V %)	$t_{\text{thickening}}$ (min, 130°C)
1	50	5.0%	0.8%	2	172
2	50	7.5%	1.0%	4	224
3	50	10.0%	1.2%	6	183
4	55	5.0%	1.0%	6	178
5	55	7.5%	1.2%	2	231
6	55	10.0%	0.8%	4	187
7	60	5.0%	1.2%	4	217
8	60	7.5%	0.8%	6	204
9	60	10.0%	1.0%	2	211
$k_1$	193	189	188	205	
$k_2$	199	220	204	209	
$k_3$	211	194	210	188	
R	18	31	22	21	

Note:  $k_1$ , average thickening time of level one;  $k_2$ , average thickening time of level two;  $k_3$ , average thickening time of level three; R: range.

terpolymer PAIN was reaction temperature(A), mass fraction of NVP (B), concentration of the initiator (C), and volume fraction of the regulator (D). Consequently, a four-factored and three-leveled orthogonal table was made to obtain the optimal reaction condition parameters. Analyzing the results of the orthogonal experiment, the optimum reaction conditions of copolymerization were obtained: wt (NVP), 7.5%; V (regulator), 4%; reaction temperature, 60°C; wt (initiator), 1%. The details were shown in Table I. The W/C was 0.44 and all the cement slurries in the test had 1.0% (BWOC) PAIN.

### Characterization of PAIN

#### FTIR analysis

The desired chemical structure of PAIN was shown in Figure 2 and the FTIR spectra of prepared terpolymer PAIN was shown in Figure 3. The characteristic bands at 3469.6  $\text{cm}^{-1}$  is stretching vibrations absorption signals corresponding to N—H in amide group, and the spectrum shows the stretching vibrations peaks characteristic for C=O in pyrrolidone group at 1706.4  $\text{cm}^{-1}$ , C=O in amide group at 1652.4  $\text{cm}^{-1}$ , and C=O in carboxy group at 1556.6  $\text{cm}^{-1}$ , and the

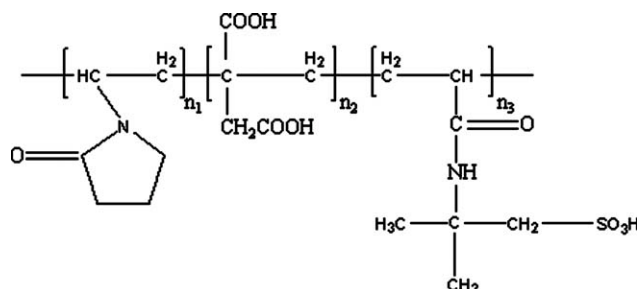
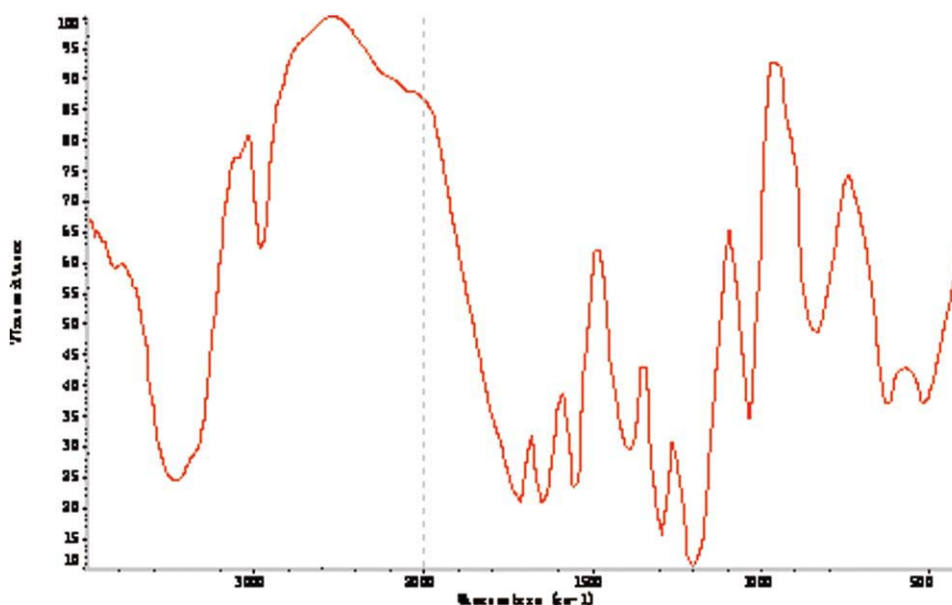


Figure 2 Desired chemical structure of PAIN.



**Figure 3** FTIR spectra of terpolymer PAIN. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

characteristic bands at  $1206.0\text{ cm}^{-1}$ ,  $1032.2\text{ cm}^{-1}$ , and  $624.7\text{ cm}^{-1}$  for stretching vibrations are corresponding to nonsymmetrical and symmetrical of S=O and S—O in sulfonic group, respectively. This proves that the target terpolymer PAIN was obtained.

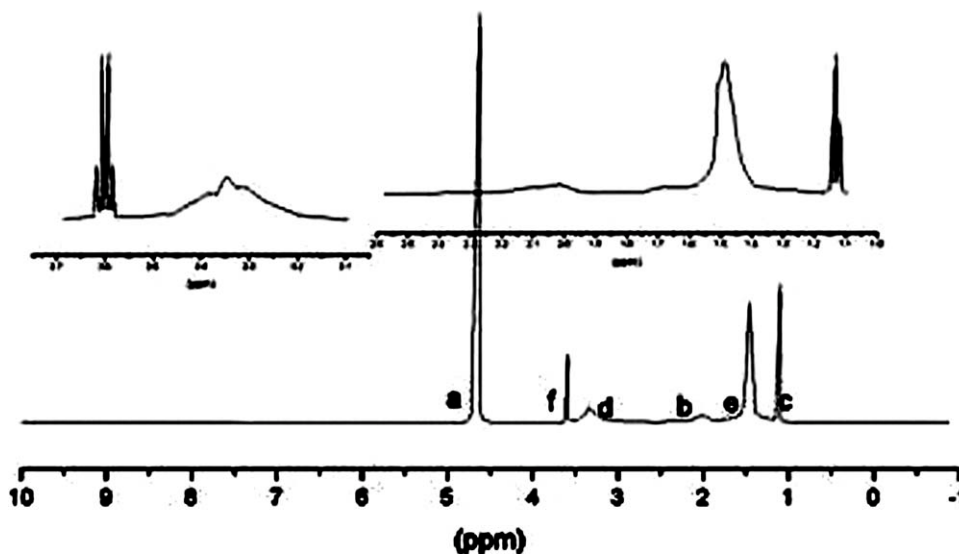
#### Proton NMR analysis

Figure 4 is the proton NMR spectrum of PAIN, and Figure 5 is the structure corresponding to the proton NMR peak. It can be seen from the Figure 4 that  $\delta 4.62$  and  $\delta 2.03$  are the vibration peaks of hydrogen of the structural unit introduced by NVP, and  $\delta 1.34$  is the vibration peak of hydrogen of the structure

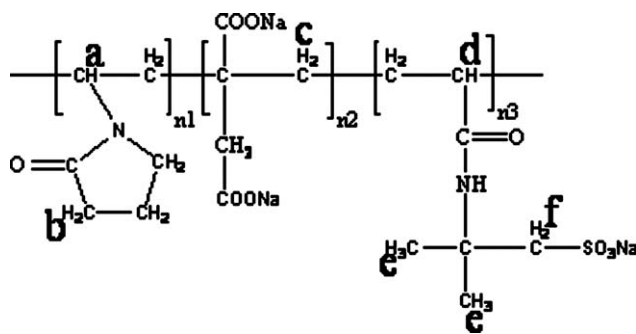
unit introduced by IA, whereas  $\delta 1.49$ ,  $\delta 3.38$ , and  $\delta 3.61$  are the vibration peaks of hydrogen of the structural unit introduced by AMPS. The polymer structure contains structural units introduced by three monomers at the same time, indicating that the terpolymer PAIN has been synthesized.

#### TG-SDTA analysis

The TG-SDTA thermogram of PAIN was shown in Figure 6. When the temperature reaches about  $350^{\circ}\text{C}$ , the differential thermal curve results in an apparent endothermic peak, whereas TG curves produce a significant weight loss, mass loss of nearly



**Figure 4** Proton NMR spectra of PAIN.



**Figure 5** Structure corresponding to the proton NMR peak.

30%, this may be caused by decomposing of secamide groups in PAIN. As the temperature is below 330°C, a little mass loss is caused by the volatilization of water, acetone, and polymers with small size. Thus, the synthetic polymer PAIN have a great heat resisting property and the structure of PAIN is stable when the temperature below 350°C, indicating that the terpolymer PAIN has met the prerequisite as a high temperature retarder. As a comparison, Su et al.<sup>13,14</sup> had both synthesized biopolymer based on AMPS, but their products were not stable in high temperature.

#### Effect of regulator on the intrinsic viscosity number of PAIN

From Table I, we had been found that the amount of regulator (isopropanol) had a greater effect on the performance of terpolymer PAIN. Figure 7 is the curve of intrinsic viscosity number of PAIN changing with the volume of regulator, indicating that intrinsic viscosity number of PAIN is decreased with

the volume increases of regulator. The intrinsic viscosity number and viscosity-average molecular weight is accordance with the Mark-Houwink equation,

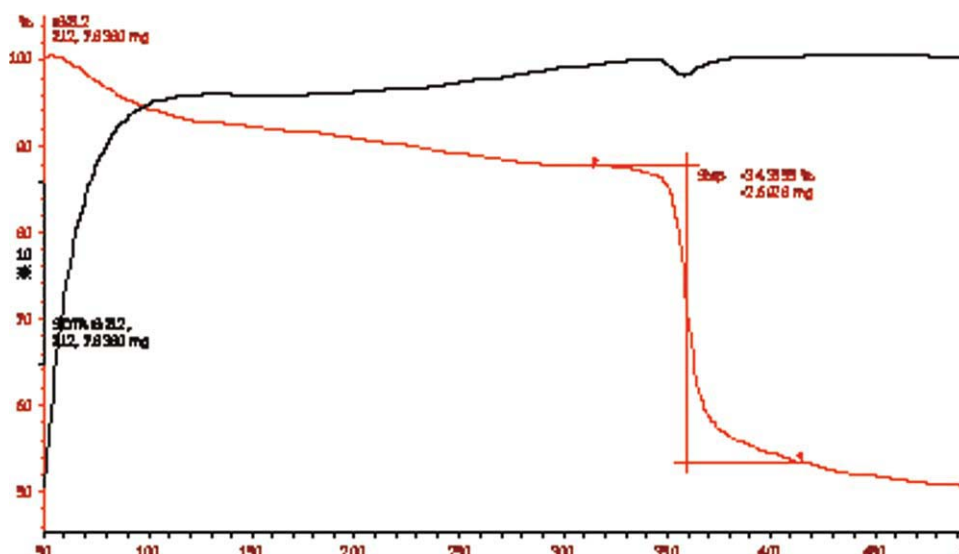
$$[\eta] = KM^\alpha.$$

In this equation, the  $[\eta]$  is the intrinsic viscosity number of polymers,  $K$  is a constant of proportionality,  $M$  is the viscosity-average molecular weight, and the  $\alpha$  is a parameter related to expansion factor. The  $K$  value is significantly influenced by temperature, while the  $\alpha$  value depends primarily on the degree of the stretch of polymer coil in solvent, generally ranging between 0.5 and 1.0. According to the literature,<sup>15</sup> the experimental parameters of methacrylic polymers at 299 K are:  $K = 1.83 \times 10^{-5} \text{ m}^3/\text{kg}$ ,  $\alpha = 0.62$ . In this article, the intrinsic viscosity is measured at room temperature in 1 mol/L sodium chloride solution, so we took  $K = 1.8 \times 10^{-5} \text{ m}^3/\text{kg}$ ,  $\alpha = 0.75$  (average of 0.5 and 1.0),  $[\eta] = 72 \text{ mL/g}$  (regulator, 4 mL) into the calculation of the PAIN, and the viscosity-average molecular weight of PAIN is obtained,  $M = 6.3 \times 10^4$ .

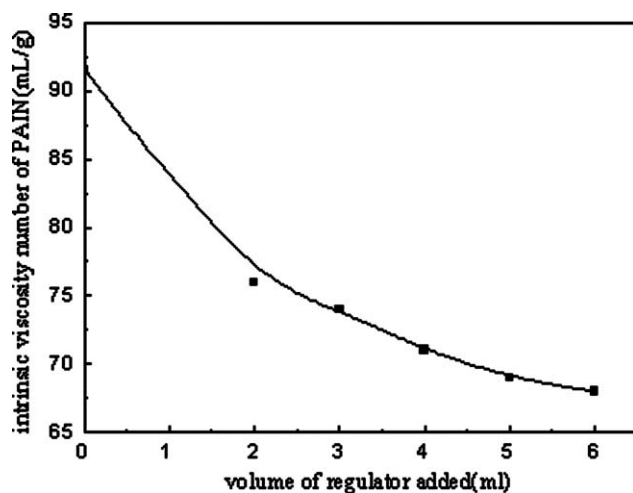
The decrease of intrinsic viscosity number virtually manifests the decrease of the molecular weight. As the chain transfer of the regulator, the molecular weights of PAIN will not too large, thus retarding performance of the product is increased.<sup>16</sup>

#### Evaluation of retarding performance

The thickening curves of cement slurries with retarder PAIN at 110 and 130°C are shown in Figure 8. The OWC-9350-type atmospheric pressure thickening instrument and OWC-9380-type supercharger thickening instrument were used in the thickening test.



**Figure 6** TG-SDTA thermogram of PAIN. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

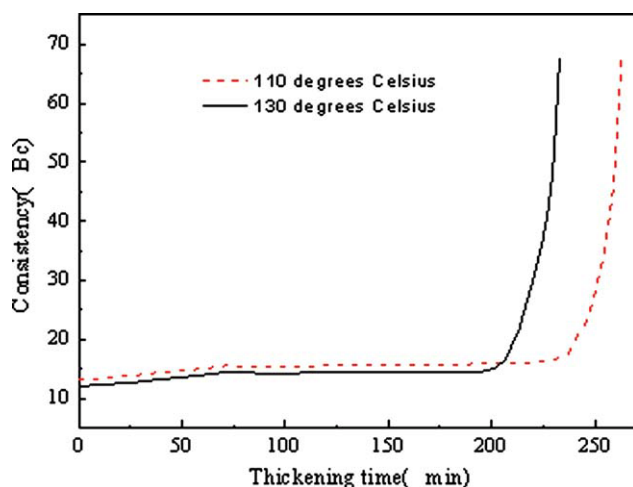


**Figure 7** Effect of volume of regulator (isopropanol) on the intrinsic viscosity number of PAIN

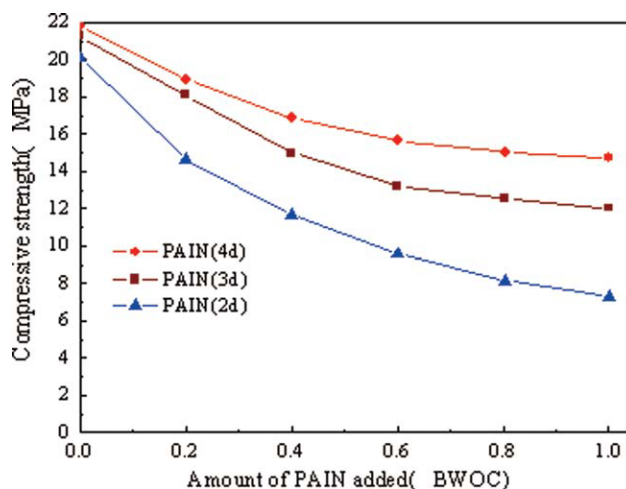
Through the test, it was found that the thickening time of the cement slurries with 1% (BOWC) PAIN was up to 256 min at 110°C and 234 min at 130°C. The transition time is very short and the curve is close to right angle, indicating that the terpolymer PAIN has an excellent retarding property under high temperature.

#### Effect of PAIN on compressive strength of cement stone

The effect of PAIN on compressive strength of cement stone under curing temperature of 90°C is shown in Figure 9. An electronic hydraulic pressure testing machine of YA-300 type was used in the experiments. It is obvious that the retarder PAIN has caused the decrease of compressive strength of cement stone. When 1% (BOWC) of PAIN is added



**Figure 8** Thickening curves of cement slurries with retarder PAIN. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



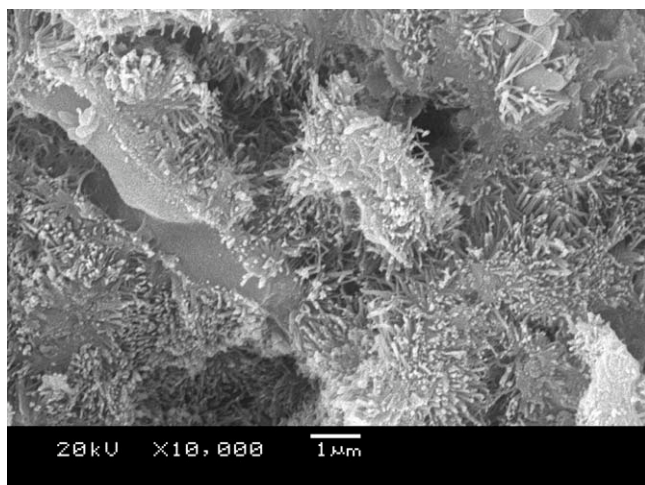
**Figure 9** Effect of PAIN on compressive strength of cement stone. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

into slurries, the compressive strength of the cement stone will decrease by 63.7% after curing 2 days, by 43.7% after curing 3 days, and by 32.1% after 4 days, indicating that the decrease caused by adding PAIN in the cement stone will be alleviated as the time going. It can be seen that the retarder mainly affects the early strength of the cement stone and has few impacts on the later strength.

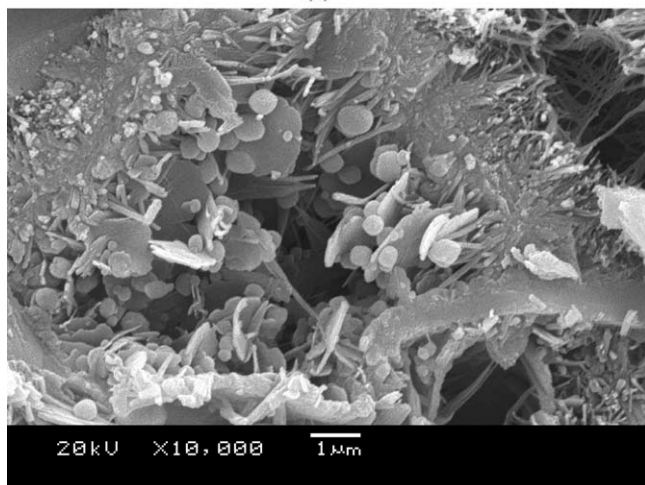
#### Analysis of retardation mechanism

Figure 10(a,b) are SEM images of the cement interface without and with PAIN, respectively. Analyzed on Figure 10(a), it can be deduced that the protective film, which coats on the particles in the slurry, was ruptured at the initial nucleation stage of cement hydration condensation. Subsequently, many nuclei of  $\text{Ca}(\text{OH})_2$  was built rapidly and grown along a-dimensional orientation, constituted hydrated calcium silicate gel with morphology of fine dense whisker group and formed network structure, then the slurry thickened. From this fine dense whisker group, it can be seen that the initial rate of the condensation reaction is very fast in this system.

It can be seen in Figure 10(b), a number of spherical, sheet, strip, and block body were appeared in addition to a small amount of whisker group because of the chelation<sup>17-20</sup> of PAIN with calcium, the mechanism of chelation was shown in Figure 11. This chelation effectively retard the formation of solid-phase gel precipitation and growth of  $\text{Ca}(\text{OH})_2$  crystal, resulting in the hydration reaction of cement slurry blocked. So, in the initial stage of hydration reaction, the nucleation rate was slowed down and the number of nuclei formed in the unit of time was reduced, which provided a time and left a space to growth of crystal nuclei. Besides, the condensation



(a)



(b)

**Figure 10** (a) Image of cement paste without PAIN. (b) Image of cement paste with 1% PAIN.

body of cement was irregular at latter stage because of the steric effect of PAIN molecular configuration. This is the first reason caused retardation of the cement slurry.

The second reason of the cement slurry retardation is that PAIN enhanced the stability of the coated film, because PAIN is a polyelectrolyte, after the carboxylic acid groups and sulfonic groups in the terpolymer chain were ionized, the terpolymer got negative charge. The terpolymer chains with negative charge could adsorb on the surface of hydrated particles and became new set ions of colloidal particles. So the thickness and stability of the hydration film were increased and the set ions with enhanced electronegativity would adsorb more calcium ions inevitably, the thickness of diffuse electric double layer was increased, the repulsive force among particles was enhanced.

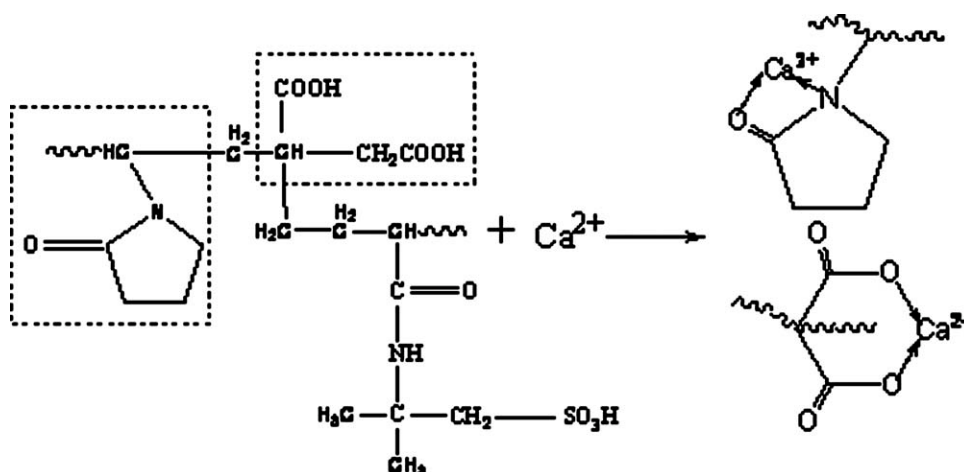
## CONCLUSIONS

The reaction conditions have a great effect on the performances of the copolymerized product. By doing the orthogonal experiment and analyzing the data in orthogonal table, the best response parameters are obtained as follows: NVP 7.5 wt %; regulator V 4%; reaction temperature 60°C; initiator 1 wt %.

Through TG-SDTA analyzing, it is found that the retarder PAIN has a good performance to resist high temperature, its chemical structure is stable below 350°C.

The intrinsic viscosity numbers are decreased with the increase of regulator's volume. The performances of product with different amount of regulators are compared, finding that the regulators can significantly affect the performances of PAIN, for they can change molecular weight and distribution of the product PAIN.

Through the thickening test, it is found that the thickening time of the cement slurries with 1% (BOWC) PAIN were up to 256 min at 110°C and 234 min at 130°C. The transition time is very short and the curve is close to right angle, indicating that the



**Figure 11** Schematic diagram of chelation between retarder PAIN and calcium ion.

terpolymer PAIN has an excellent retarding property under high temperature.

The retarder PAIN would cause the decrease of compressive strength of cement stone, but it mainly affects the early strength of the cement stone and has few impacts on the later strength.

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