

# Preparation and Application of a Series of Novel Anionic Acrylamide Polymers with Cyclodextrin Sides

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**ABSTRACT:** In this article, the synthesis and characterization of a new class of macromolecule water-soluble polymers with cyclodextrin sides were presented, which possess molecular recognition function. The polymer composed with three functional monomers was investigated through an infrared spectrometry and a scanning electron microscope. Then, the rheological properties and the interaction with surfactant of this series of polymer samples were evaluated and compared with polyacrylamide to prove that they have superior rheology performance. Also,

through the adsorption experiment it can be seen that the polymer has excellent performance in polymer flooding, and it can effectively reduce over 20% of the surfactant loss caused by stratum absorption in the process of polymer/surfactant flooding. These have laid a theoretical foundation for its application to enhance oil recovery. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 953–961, 2011

**Key words:** rheology; acrylamide-cyclodextrin polymers; surfactants; enhance oil recovery; ost-guest systems

## INTRODUCTION

At present, the water-soluble polymers have been widely used in various areas of the national economy, such as oil production, sewage treatment, chemical industry, pharmaceutical industry, and so on. polyacrylamide (PAM) flooding technology is an important way to enhance oil recovery, but the effect is limited, because such polymers cannot improve the interfacial tension of the oil-water-rocks in the process of flooding. Thus, it has become a research spotlight to introduce surfactant functional groups into PAM polymer.

Host-guest chemistry theory presents that molecules with cage or cup-type structure can include guest molecules.<sup>1–4</sup> In the study of the host compounds, whose structures have been confirmed cyclodextrin (CD) takes up a large proportion, and its inclusion effect for surfactant has been proved to be relatively stable.<sup>5</sup> So far, the subject of how to avoid surfactant loss caused by stratum absorption through the inclusion function of CD has been studied by our group, and many good achievements have been got-

ten.<sup>6,7</sup> Some previous researches also revealed that the CD derivatives had an obvious effect of viscosification and could effectively enhance the flooding effect of polymers.<sup>8–10</sup> However, because the production of  $\beta$ -CD has been industrialized and the cost of which is low, furthermore, the modification methods of  $\beta$ -CD are relatively more and mature, and in this article  $\beta$ -CD is chosen for study.

To introduce the superior property of CD into polymers a novel molecular was designed, and the synthetic process of which is shown in Figure 1.

Besides, an ideal model was built to show the process of enhancing oil recovery through the synergic action between this series of polymers and surfactant, as is shown in Figure 2.

It can be seen from the model that, after the inclusion compounds, which were composed by the polymer and surfactants, were injected into the stratum, they interacted with oil phase molecules, which then replaced the surfactants in CD cavities. While the released surfactants moving into oil phase and reacting on the oil-rock interface, the crude oil was broken away from rock surface. Then the oil recovery was improved with polymer flooding.

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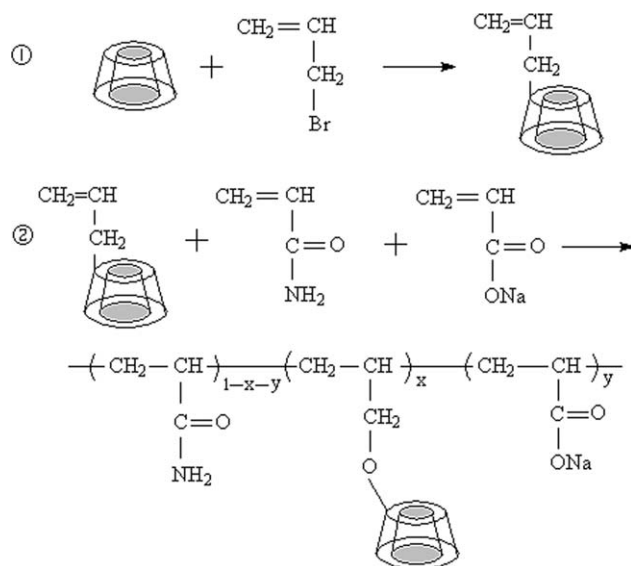
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## EXPERIMENTAL SECTION

### Materials

In this work, acrylamide (AM), acrylic acid (AA), potassium persulfate, sodium bisulfite, sodium



**Figure 1** The synthetic process of this novel polymer.

hydroxide, disodium EDTA, hexadecyl trimethylammonium chloride (cationic surfactants), and anhydrous-ethanol were used as materials. All of them (analytical grade) were obtained from Kelong chemical reagent factory (Chengdu, China). The oil sand was obtained from Liaohe oil field, which was used in the adsorption experiment.

### Synthesis of allyl- $\beta$ -CD

The appropriate solvent containing a certain amount of  $\beta$ -CD was prepared in a round-bottom flask equipped with a mechanical stirrer, and sufficient sodium hydroxide as a catalyst was added with vigorous stirring until completely dissolved. Then a certain amount of allyl bromide was slowly added into

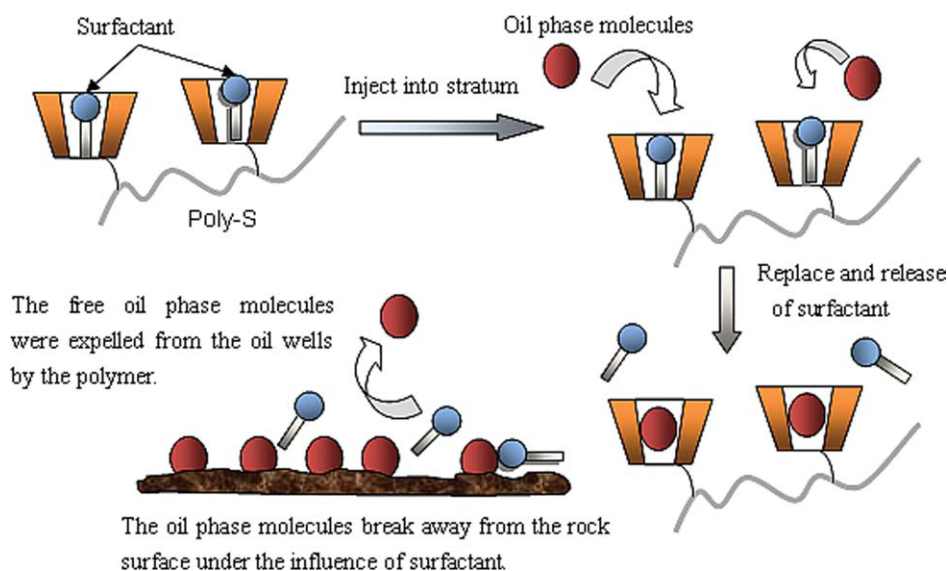
the flask in ice water bath (0–10°C), reacted for 48 h. Finally, white powder-like products were got after washing with acetone and vacuum filtration and were preserved under sealed and cool conditions, because of its high water absorbing nature.<sup>11,12</sup>

### Synthesis of Poly-S

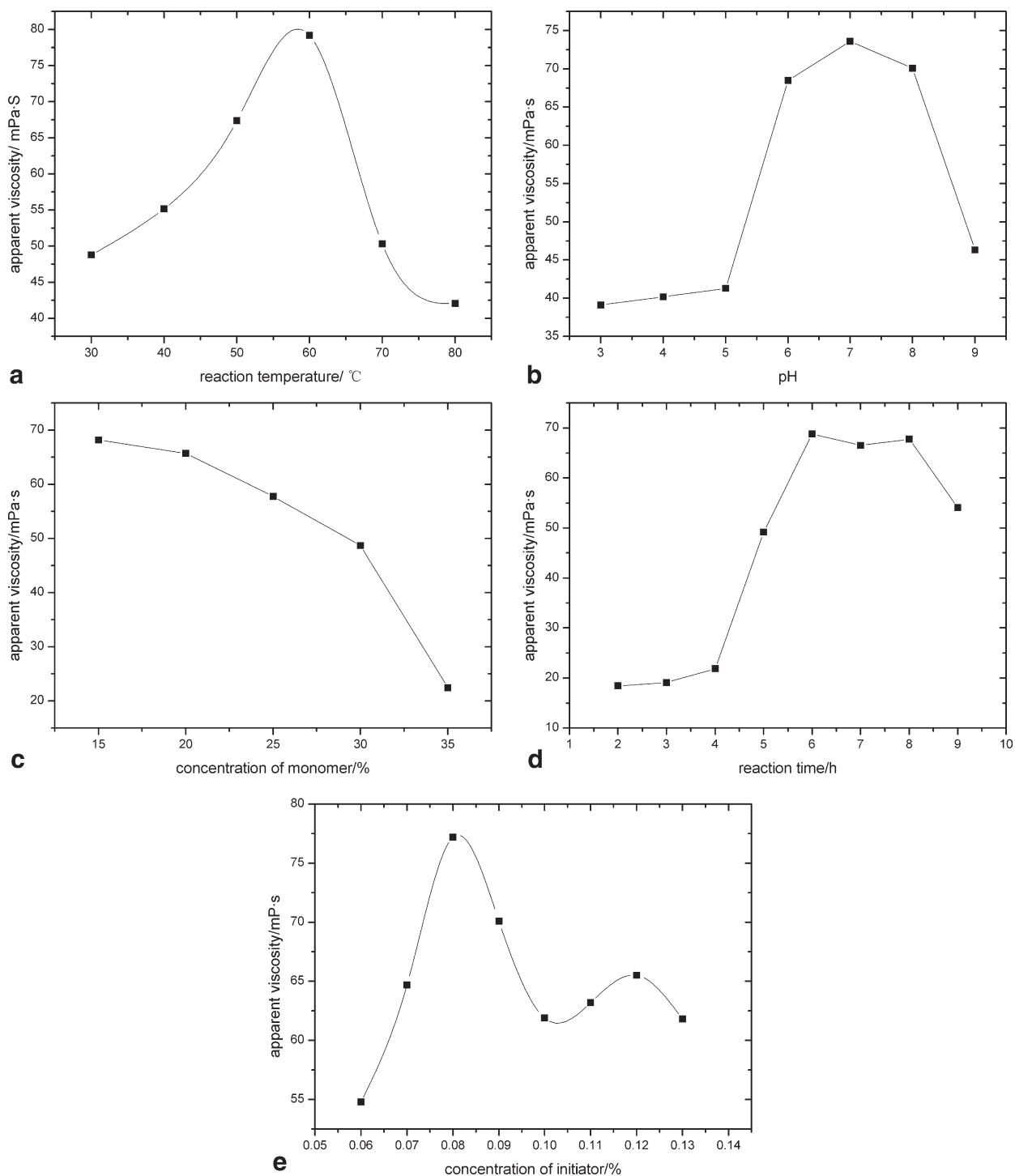
The aqueous solutions containing different percentage of allyl- $\beta$ -CD, sodium acrylate, and AM were prepared in four round-bottom flasks equipped with mechanical stirrers. The molar ratios of the aforementioned substrates were 1 : 5 : 13, 1 : 5 : 39, 1 : 5 : 117, and 1 : 5 : 351, respectively. Followed by the addition of an appropriate amount of chelating agent (EDTA), oxidants (potassium persulfate), and reluctant (sodium bisulfate) to each flask with vigorous stirring and the ratio among them was 4 : 1 : 1. Then transparent gelatinous material appeared after reacting for 4–6 h, which was washed for several times with absolute ethanol to precipitate a white block solid. The solid was further dried in the oven at 50°C. Then the products from the four flasks were named as Poly-S-1, Poly-S-2, Poly-S-3, and Poly-S-4, respectively. Furthermore, the optimal experimental conditions of these reactions were defined and evaluated through apparent viscosity experiments of products. The experimental results under different reaction conditions (reaction time, pH value, etc.) are shown in Figure 3(a–e). After a comprehensive analysis, the optimal results are presented in Table I.

### Scanning electron microscope (SEM) experiment

To observe the structure, the surface morphology and the size of the Poly-S clearly, a PHILPS-XL30



**Figure 2** The ideal model of synergic action between CD-polymer and surfactant flooding. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** a) Influence of reaction temperature, (b) influence of pH, (c) influence of the concentration of monomer, (d) influence of reaction time, and (e) influence of the concentration of initiator.

**TABLE I**  
The Optimal Conditions of the Polymerization

Reaction temperature	System pH value	Concentration of monomer	Time
50–60°C	7–8	15–20%	6h
Content of initiator	The ratio of initiators	Molar ratio of monomers	
0.08%	4 : 1 : 1	1 : 5 : 117	

scanning electron microscopy was used. Take the case of Poly-S-3, the structure and composition were analyzed.

### Infrared (IR) experiment

Poly-S-3 and sodium acrylate/acrylamide polymer were analyzed with a 170SX IR spectrometer on KBr disks, produced by Nicolet (Thermo Fisher Scientific, Shanghai, China), to prove this series of polymers was obtained by polymerization of the three monomers we used. The resolution of this spectrometer is  $4\text{ cm}^{-1}$ .

### Rheological experiments

In this study, the rheological properties of the Poly-S and PAM were evaluated and compared through rheological experiments of salts tolerance, temperature tolerance, and the nature of viscosification. The performance comparison between Poly-S and PAM was carried out by investigating apparent viscosity variations with mineralization and temperature changing. To research the interaction between polymer and surfactant, surface tension and viscosity of the mixed system were also measured. The surface tensions of the mixtures were measured through ring-detachment method using a ZL-3000 automated tensiometer with a precision of  $\pm 0.1\text{ mN/m}$ . Viscosity measurement is performed with NDJ-8S viscometer, the measurement error of which is  $\pm 5\%$ , and the rotor speed is 60 rpm. The tensiometer and viscometer were adjusted through ultrapure water and standard silicon oil (Brookfield) at  $25^\circ\text{C}$ , respectively.

### Adsorption experiment

Under normal circumstances, the surfactant flooding cannot bring about the best results. The consumption of surfactant was increased, because of the adsorption effect of the stratum.<sup>13</sup> But now, the CD cavity can effectively protect the surfactant against the adsorption of stratum, according to the basic theory of inclusion function of the CD cavity to cationic surfactants.<sup>5</sup> The law of stratum adsorption to the mixed solution of surfactant and Poly-S was investigated through adsorption experiment. At first, the absorbance value of the prepared solution of known concentration was measured, and the absorbance coefficient of this system was calculated based on Lambert-Beer law [eq. (1)].

$$A = KCL = -\log \frac{I}{I_0} \quad (1)$$

where  $A$  is absorbance,  $K$  is absorbance coefficient,  $C$  is the concentration of solution, and  $L$  is optical path length.

Then the absorbance value of the solution, which had accomplished the adsorption test was measured, and the ending concentration of the solution was also calculated based on Lambert-Beer law. Finally, the adsorption quantity of each solution was calculated with adsorption equation. The measurement of absorbance in this part was carried out using UV-3802 UV spectrometer produced by UNICO of China. Furthermore, the excellent application prospects of such polymer in the field of multiphase mixed flooding were illustrated through the analysis of results.

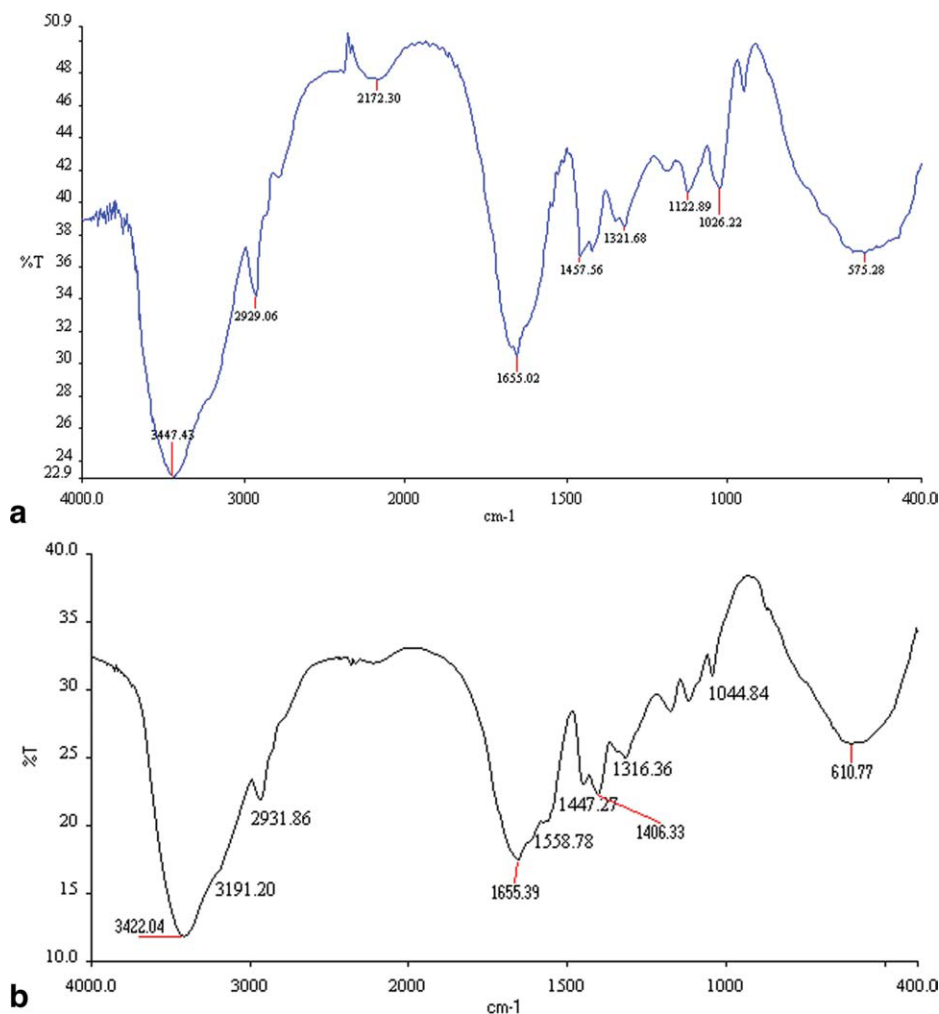
## RESULTS AND DISCUSSION

### Structure of Poly-S

In the case of Poly-S-3, from its IR image [Fig. 4(a)], it can be found that  $3450\text{ cm}^{-1}$  is the stretching vibration peaks of N—H bond in the amide groups ( $-\text{CONH}_2$ ),  $1655.02\text{ cm}^{-1}$  is the stretching vibration peaks of C=O bond in  $-\text{CONH}_2$ , and both of them prove that this compound contains AM and acrylic acid sodium structure. Besides,  $3400\text{ cm}^{-1}$  is the stretching vibration absorption peak of O—H bond in CD hydroxyl,  $1026.22\text{ cm}^{-1}$  is the stretching vibration peaks of C—O bond in CD hydroxyl,  $1180.00\text{ cm}^{-1}$  is the stretching vibration peaks of C—O—C bond in CD molecules,  $930.00\text{ cm}^{-1}$  and  $575.28\text{ cm}^{-1}$  are skeleton vibration of CD. As we know, the vibration peaks will displace because of the interaction between functional groups. So the two peaks in  $3450\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  are overlapped in  $3447.43\text{ cm}^{-1}$ . Through the relative analysis with the IR image of sodium acrylate/acrylamide polymer [Fig. 4(b)], it can be indicated that this binary polymer has no skeleton vibrations of CD in  $930.00\text{ cm}^{-1}$  and  $575.28\text{ cm}^{-1}$ . Also, the stretching vibration peaks of C—O—C bond in CD molecules in  $1180\text{ cm}^{-1}$  is absent. In addition, the binary polymer possesses all of the peaks of AM and acrylic acid sodium, and this agrees well with the reports.<sup>14–16</sup> This result indicates that the typical structure of CD is not present in the binary polymer. Thus, a conclusion can be reached that Poly-S-3 contains the structures of CD, AM, and sodium acrylate. This polymer sample is the product of goal.

### Surface morphology of Poly-S-3

Figure 5(a) shows the surface morphology of Poly-S-3 under SEM at 50 times zoom. Figure 5(b,c) are enlarged images at 500 and 1000 times zoom, respectively. These two images indicate that the sample is a typical gel-network structure. This is possible because several —OH groups of  $\beta$ -CD have been replaced by allyl groups, and then polymerization of



**Figure 4** a) IR image of Poly-S-3 and (b) IR image of sodium acrylate/acrylamide polymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

allyl- $\beta$ -CD with AM or acrylic acid sodium happens, which brings about the formation of supramolecular chain aggregates. Other possible reasons may be the intermolecular or intramolecular association and cross-linking reaction between gels. These behaviors lead the formation of three-dimensional network structure, which contains a lot of cavities.<sup>17,18</sup> Figure 5(d) shows the cross-section morphology of the polymer through which it can be discovered that the sample possesses a smooth surface.

## Rheology experiments

### Salt resistance of polymers

The salt solutions and water solutions of PAM and Poly-S (Poly-S-1, Poly-S-2, Poly-S-3, and Poly-S-4) were prepared with deionised water, respectively. The concentration of polymer were all 2.0 g/L, and the salinities of salt solutions were all  $1.6 \times 10^5$  mg/L. Every salt solution contains  $\text{Ca}^{2+}$  of 2000 mg/L,  $\text{Mg}^{2+}$  of 1000 mg/L, and the rest are  $\text{Na}^+$  and  $\text{Cl}^-$ . Then the

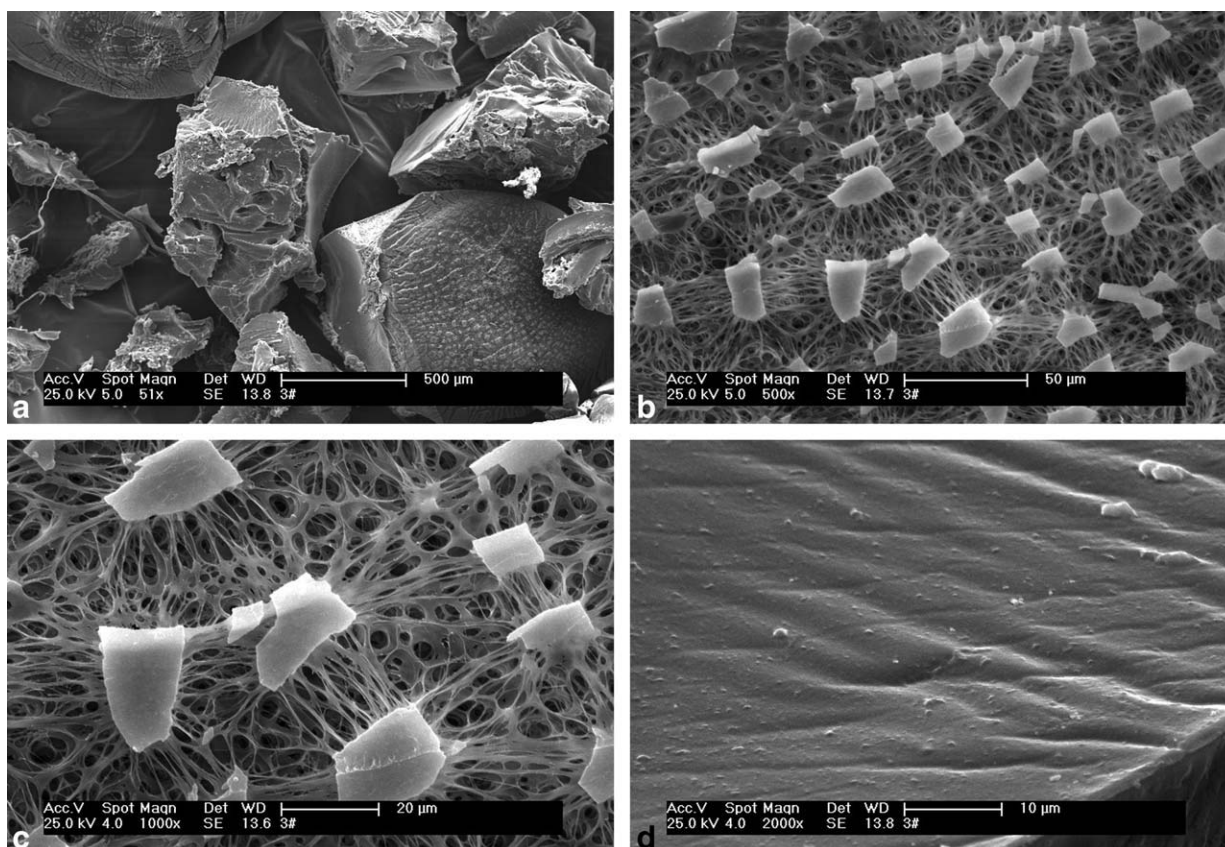
viscosities of salt solutions and water solutions were measured, and the rate of viscosity retention of these polymers in the salt solution at 25°C was calculated.

Generally, due to the salt-sensitivities of polymers, their viscosities change obviously with the salinities of systems changing. In this article, it can be illustrated from the results in Table II that the rate of viscosity retention of Poly-S was over six times higher than that of PAM when the salinity of solution system changes.

### Temperature tolerance of polymers

The aqueous solutions of Poly-S-3 and PAM were prepared respectively, and the concentrations of them were both 3000 mg/L, and the salinity were both  $1.6 \times 10^5$  mg/L, then the viscosities were measured and the rates of viscosity retention of each polymer at temperatures of 25, 50, 75, and 90°C were calculated.

As we know, the interaction between molecules will be strengthened and the viscosity will be



**Figure 5** a) SEM image of Poly-S-3 at 50 times zoom, (b) SEM image of Poly-S-3 at 500 times zoom, (c) SEM image of Poly-S-3 at 1000 times zoom, and (d) SEM image of Poly-S-3 at 2000 times zoom.

increased with temperature rising. But if the temperature continues to increase, the structure of polymer chain will be changed (break, etc.). This will lead to a huge viscosity loss of polymer solutions.<sup>19</sup> From the results in Table III, it can be seen that the Poly-S-3 had a higher rate of viscosity retention than PAM. It means that the polymers we synthesized have more powerful abilities to maintain their structures when the temperature varies.

#### Nature of viscosification

The aqueous solutions of Poly-S and PAM were prepared at different concentrations, and then the apparent viscosity of each polymer solution was measured. The change trends are shown in Figure 6.

**TABLE II**  
Comparison of Salts Tolerance

Polymer	$\eta_{\text{water}}$ (mPa·s)	$\eta_{\text{salt}}$ (mPa·s)	Rate of viscosity retention (%)
PAM	112.45	11.92	10.6
Poly-S-1	77.51	48.62	62.73
Poly-S-2	89.43	61.32	68.57
Poly-S-3	96.72	73.83	76.33
Poly-S-4	107.19	78.89	72.67

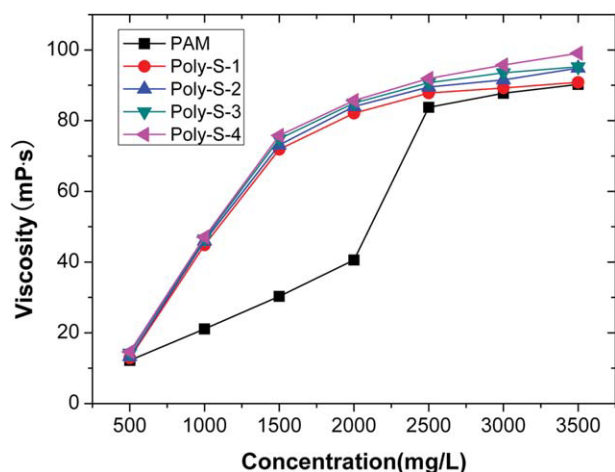
**TABLE III**  
Comparison of Temperature Tolerance

Polymer	$\eta_{25^{\circ}\text{C}}$ (mPa·s)	Temperature ( $^{\circ}\text{C}$ )	$\eta$ (mPa·s)	Rate of viscosity retention (%)
PAM	31.85	50	24.91	78.21
		75	18.55	58.24
		90	7.13	22.39
Poly-S-3	44.74	50	38.62	86.32
		75	32.59	72.84
		90	27.41	61.27

It can be seen from Figure 6 that the viscosity and concentration of polymer solutions had a linear relationship. Simultaneously, the viscosity of Poly-S took on a remarkable increase with a low concentration and tended to maintain a trend of rising slowly when the concentration was higher than 2000 mg/L. But there was no obvious increase in the viscosity of PAM solution until the concentration exceeded 2000 mg/L. This shows that the viscosification of Poly-S is stronger than that of PAM solution.

#### Interaction between polymer and surfactant

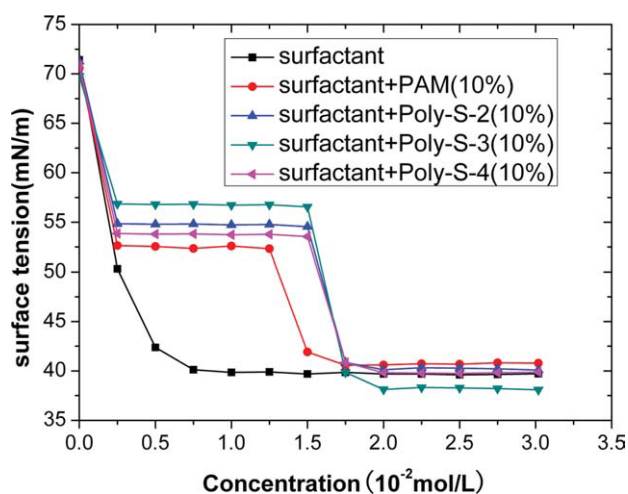
Several different aqueous solutions were prepared with equivalent surfactant and 10% PAM or 10%



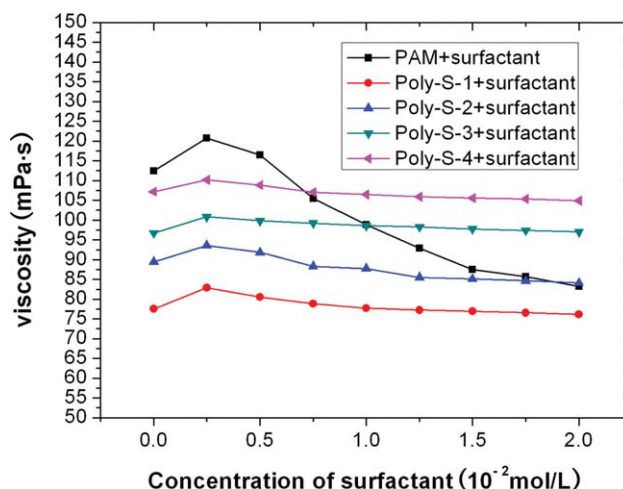
**Figure 6** Viscosity curves of polymers at different concentrations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Poly-S, and then the surface tension and viscosity of each solution at 25°C was measured. The results are shown in Figures 7 and 8.

It can be indicated from Figure 7 that, Poly-S and PAM can affect the process of the surface tension of solution being reduced by surfactants. Compared with the single surfactant solution, there was a plateau in surface tension of the mixed solution at appropriate concentrations, and a lower value was reached finally. Also it can be known that the plateau trend of Poly-3-surfactant solution continued longer, and its final surface tension value was lower than the other solutions, which means the Poly-3 has a better performance. The most likely cause is shown in Figure 9. With the concentration of the Poly-S-surfactant mixture increasing, there was a clear plateau in the surface tension change trend. The reason is



**Figure 7** Surface tension curves of surfactant and surfactant-polymer mixed solutions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8** Viscosity curves of polymer-surfactant mixed solutions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

that the prepared polymer has brought in CD monomers. The CD cavity has surfactant inclusion function, which makes part of the surfactants come into the cavity and unable to show the surface activity. But PAM does not have such function. Besides, the formation of the surfactant micelles on polymer surface is another reason.

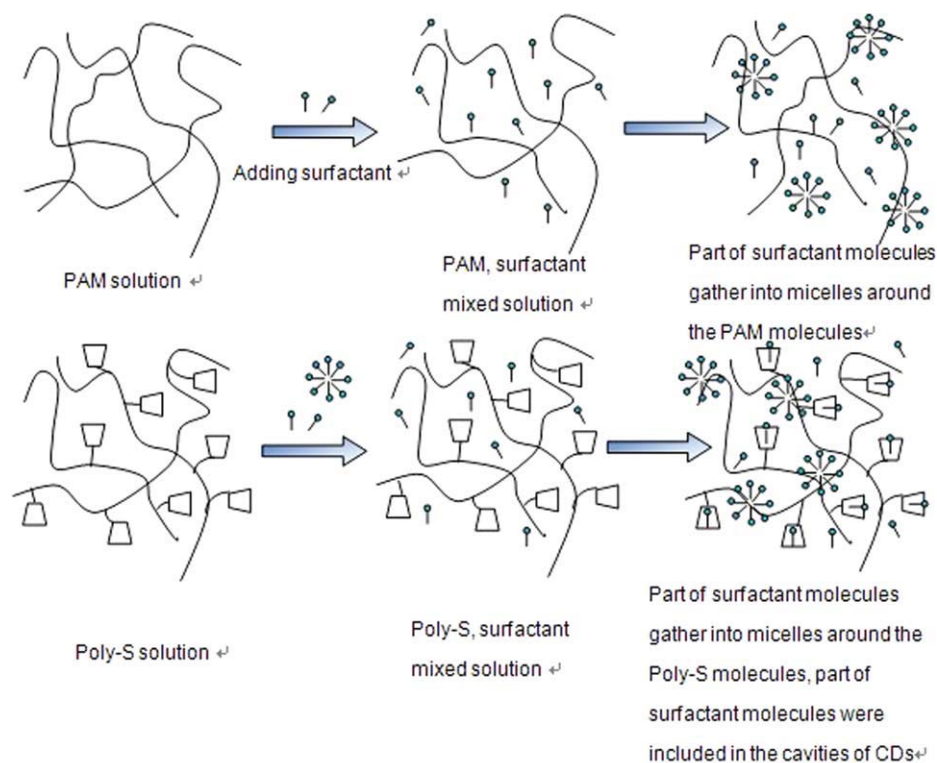
Figure 8 shows that this series of polymers can maintain viscosity character better than PAM in mixed solutions with different concentrations of surfactant at 25°C, which proves the extensive application prospects of this polymer in the polymer/surfactant flooding.

### Adsorption experiment

In the study, PAM, Poly-S-3, and cationic surfactant were prepared into aqueous solutions at different concentrations respectively. Oil sands were milled into 80–100 screen mesh as adsorbent, and then 100 g of them were added into every cone-shaped bottle of the 0.5 L prepared solution. The solution and the oil sands were mixed by a constant temperature shaker under the speed of 150 r/min for 24 h. Ultimately, oil sand was removed by high-speed centrifuge, and the concentration of upper clear liquid was determined by UV spectrophotometer. The adsorbance of the stratum to cationic surfactants was calculated according to eq. (2).<sup>20</sup> The result is shown in Figure 10.

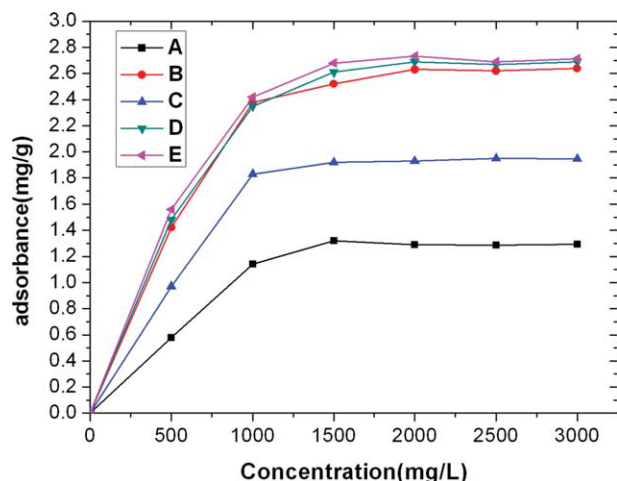
$$A = \frac{(\rho_0 - \rho_x)V}{m} \tag{2}$$

where  $A$  is adsorbance,  $\rho_0$  is the initial concentration of solution,  $\rho_x$  is the ending concentration of solution,  $V$  is volume of solution, and  $m$  is the weight of oil sand.



**Figure 9** The model of interaction between polymer and surfactant. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Figure 10 presents the adsorbance of surfactant in the different solutions A, B, C, D, and E. E was cationic surfactant solution, D and B were mixed solutions composed of PAM and surfactant, which were stirred for 1 minute (D) and 1 h (B), C and A were mixed solutions composed of Poly-S-3 and surfactant, which were stirred for 1 minute (C) and 1 h (A) (the volume ratio of polymer to surfactant was 1 : 1). It can be seen that the adsorbance was significantly reduced through adequate mixing and inclu-



**Figure 10** Curves of adsorption of oil sand. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

sion action between surfactant and Poly-S-3 with the reduction ratio of 20%. So it can be indicated that such series of polymer has broad application prospects in the polymer/surfactant mixed flooding.

## Conclusions

In this article, the synthesis and characterization of a series of new AM polymers with CD sides were investigated. Through SEM, IR, rheological and adsorption experiments, it can be found that AM/NaAA/Allyl- $\beta$ -CD polymer can be synthesized by allyl- $\beta$ -CD, sodium acrylate, and AM under the effect of initiator through radical polymerization. It is proved that this series of polymers have excellent salt tolerance, temperature tolerance, the nature of viscosification, and excellent interaction with surfactant through the rheological experiments, especially the polymer whose monomer molar ratio is 1 : 5 : 117 (Poly-S-3). It can be also found that the CD sides provide the polymer with a superior inclusion property for surfactants, which can effectively avoid the surfactant loss, caused by adsorption of stratum, and will significantly improve the new polymer's ability to enhance oil recovery.

## References

- Martin, E. M.; Del, V. *Process Biochem* 2004, 39, 1033.
- Miwa, K.; Nashimoto, E.; Tatsuro, T.; Morisaki, Y.; Mitsuaki, K.; Hideaki, H. *Tetrahedron Lett* 2006, 47, 1927.



3. Ruxandra, G. *J Controlled Release* 2006, 111, 316.
4. Prabakaran, M.; Mano, J. F. *Carbohydr Polym* 2006, 63, 153.
5. Funasaki, N.; Ohigashi, M.; Hada, S.; Neya, S. *Langmuir* 2000, 16, 383.
6. Wenju, L.; Changjun, Z.; Ying, L. *J Appl Chem* 2008, 25, 1057.
7. Wenju, L.; Changjun, Z.; Ying, L. *Oilfield Chem* 2008, 25, 74.
8. Anna-Lena, K.; Neda, B.; Hans Kristian, K.; Kaizheng, Z.; Bo, N. *Eur Polym J* 2008, 44, 959.
9. Noelle, M. G.; Horacio, N.; Estelle, R.; Catherine, A.; Bernard, S. *Eur Polym J* 2002, 38, 649.
10. Noelle, M. G.; Flavie, B.; Estelle, R.; Catherine, A.; Bernard, S. *Colloids Surf A* 1999, 155, 177.
11. Zhang, R.; Zhao, B. *Synth Chem* 2003, 11, 76.
12. Zhang, J. *J Chi Zhou Teach Coll* 2001, 15, 17.
13. Nedjhiouia, M. *Desalination* 2005, 185, 543.
14. Xie, D.; Zhang, X.; Ji, H. *J Northeast Normal Univ* 1988, 3, 75.
15. Fuqiang, Z.; Zengjian, G.; Hong, G.; Yanchi, L.; Li, R.; Lei, S.; Lixin, W. *Polym Bull* 2005, 55, 419.
16. Wang, K.; Zhou, S. *Chem Intermed* 2009, 12, 49.
17. Chen, X. Structure and formation mechanism of supramolecular aggregates with  $\beta$ -cyclodextrin, A master's degree thesis, Shanxi Normal University, 2007.
18. Yan, L. Study on construction and formation mechanism of new supramolecular aggregates of ferrocene derivatives with  $\beta$ -cyclodextrin, A master's degree thesis, Shanxi Normal University, 2007.
19. Sun, J.; Wang, Z. *Adv fine petrochemicals* 2003, 6, 33.
20. Yao, T.; Yao, F.; Li, J. *Oil drill prod Technol* 2008, 30, 82.