Investigation of the degradation and stability of acrylamide-based polymers in acid solution: Functional monomer modified polyacrylamide

Yuxin Pei a,*, Liqiang Zhao a,**, Guangyan Du b, Nianyin Li a, Kun Xu a, Hanjie Yang c

a State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, People's Republic of China
b Oil & Gas Field Applied Chemistry Key Laboratory of Sichuan Province, Southwest Petroleum University, Chengdu 610500, People's Republic of China
c Shu'nan Gas Field, Petrochina Southwest Oil & Gas Field Company, Luzhou 646000, People's Republic of China

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Acrylamide copolymers are often used as acidizing diverting and thickening agents for their advantageous thickening, flocculation, adhesion and resistance reduction properties. Experimental results indicate that the acid concentration greatly affects the properties of acrylamide polymers, which varies from results reported by other researchers. Considering the theoretical and field application value of the present study, four comparable acrylamide-based polymers were synthesized, and their macro- and micro-changes as well as the related changes in viscosity and molecular weight were studied in high-concentration hydrochloric acid. A proposed mechanism of acrylamide copolymer stability and degradation is provided, and further suggestions are made for the modification of acrylamide copolymers.

1. Introduction

Acrylamide copolymers are water-soluble polymers that are insoluble in most organic solvents, and demonstrate advantageous thickening, flocculation, adhesion and resistance reduction properties. Acrylamide copolymers reduce friction against the solution liquid, and can be divided in categories based on their ionic characteristics into non-anion, anion, cation, or zwitterionic compounds [1,2]. Acrylamide copolymers are primarily used in oil production for mud drilling to enhance oil recovery, and are thus widely used in drilling, well completion, cementing, fracturing and acidizing in oil exploration, as they can increase viscosity, filtration loss, flow regulation, gel, diversion, profile modification and other functions [3–11].

Acidizing is an important stimulation measure which increases injection wells, depends on the acidic dissolution of rock and contributes to hydraulic action that improves substance permeability. One of the most important problems is the effective placement of acid to achieve diversion and thickening [12–15]. Acrylamide copolymers with cationic or anionic monomers exhibit good thickening, acid resistance, high-temperature stability, shear resistance and salt resistance properties, which induce excellent performance in acid thickening agents (acid densifiers or acid-gelling agents) [16–19] and acid diverting agents [20–29]. Acid thickeners include xanthan polymers (XP), guar gum (GG), hydroxyethyl cellulose (HEC), carboxymethylhydroxyethyl cellulose (CMHEC), polyacrylamide (PAM), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), acrylamide/sodium-2-acrylamido-2-methylpropane sulfonate copolymer (PAM/AMPS), and cationic surfactants that thicken acid when used in high concentrations. Among the various acid thickeners, acrylamide polymer products are the most frequently developed and applied, and thus are some of the most important acid thickeners [1,18,19].

It is well known that acid systems used in acidizing employ high concentrations of hydrogen ions (hydrochloric acid...
concentration up to 20 wt%), which pose great challenges to the stability of acrylamide-based polymers.

Scheirs [30] reported that the “chemical attack of polymers is due to an acid- (or base-) catalyzed reaction rather than to a direct molecular degradation by the acid (or base) alone” and provided an example of polyamide (nylon) exposed to HBr conditions. It was also reported that HBr acts as a catalyst for the hydrolytic scission of amide bonds, resulting in a scission and MW chain reduction. Muller et al. [31], proposed that polyacrylamides would hydrolyze under slightly acidic conditions (pH = 4), and reported that the molecular weight of the polymer remained relatively stable during hydrolysis. Thomas et al. [32], investigated the effects of different pH conditions and reaction times on the hydrolysis process. Results indicate that low pH conditions and long reaction times allow for nearly complete hydrolysis of all amide groups. It was also observed that the reaction involves the nucleophilic addition of water to the protonated amide group. Marcus et al. [33], summarized the detailed properties and degradation of polyacrylamide under chemical attack. They proposed that most chemistry is concerned with the reactivity of the amide group, which conveniently restricts the current discussion to relatively mild reactions to which the polymers would be exposed in day-to-day applications. Choi [34], et al., systematically studied the properties of hydrolyzed polyacrylamide, also known as pH-sensitive polymer (pH-triggered polymer). They discovered that the viscosity of hydrolyzed polyacrylamide exhibits pH dependence as characterized by transition zones (at pH = 3 and pH = 6), where the viscosity suddenly changes. This is because the hydrogen ions adsorb and dissociate from the carboxyl functional groups, a discovery which has significant application potential [35,36]. Zhang et al. [16], synthesized the polymer thickening agent DXGY-1, which is a cationic polyacrylamide. Its viscosity retention ratio in 12% HCl + 3% HF reached 82%. Liu et al. [17], synthesized a copolymer from AM, DMDAAC, and AMPS monomers and a cationic monomer X. As an acid thickening agent, the viscosity retention ratio of the copolymer in 20 wt% HCl reached 90%. Al-Taq et al. [20], synthesized an acrylamide-based polymer containing less than 5 mol% of hydrophobic groups. This associative polymer can be used for acid diversion and water control, and has been widely used in Saudi Arabia [21–29].

The works mentioned above primarily focus on a pH range in which the hydrogen ion concentration is less than 10^{-1} mol/L; however, acidizing stimulation often involves hydrochloric acid concentrations of up to 20 wt%, which is 50 times greater than that of pH = 1. Furthermore, much research has synthesized acrylamide-based polymers for use as acid densifiers and diverters, but little research has investigated the apparent viscosity decrease or whether the acid induces polymer chain scission or simple electrostatic interaction. This work investigates the mechanism of acrylamide copolymer stability and degradation in high concentrations of hydrochloric acid. Based on the aqueous solution polymerization method, a proportion of charged monomers occupying 10 wt% were placed in the same initiator (redox initiator system), and four types of acrylamide copolymer were synthesized. Hydrochloric acid was then added to the polymer aqueous solutions of certain viscosities at masses of 1 wt% and 10 wt%. Three methods were selected to simultaneously observe the resulting hydrolysis and degradation.

(1) Observation of changing solution properties;
(2) Measurement of the relationship between apparent viscosity and time after addition of different concentrations of acid;
(3) Observation of changes to the polymer chains by SEM.

Finally, a comprehensive analysis of the experimental results clarified the relationship between the functional monomer modified acrylamide copolymers and their acid resistances.

2. Experimental methods

2.1. Materials

The acrylamide, acrylic acid, 2-acrylamide-2-methyl propane sulfonic acid, allyl ammonium chloride, allyl chloride, ethyl acetate, p-toluene sulfonic acid, hydroquinone, cyclohexane, sodium hydroxide, and hydrochloric acid used in the experiment (36%–37%) were all of AR grade (Kelong Chemical, Chengdu, China).

2.2. Polymerization methods and characterization

In order to obtain four comparable acrylamide-based polymers, identical polymerization temperatures, initiator systems, initiator systems (ammonium persulfate and sodium bisulfite) and contents, functional monomer proportions, and water solutions of identical pH were employed. The specific polymerization methods are described as follows.

(1) PAM. Acrylamide was dissolved in distilled water to compose a 10% (w/w) monomer solution. The monomer solution was then poured into a four-necked flask, which was then filled with nitrogen. The aqueous ammonium persulfate and sodium bisulfite aqueous solutions were then dripped through two constant pressure funnels as a redox initiation. The system was maintained at 40 °C in a water bath for 8 h, and the resulting samples were stored for use.

(2) HPAMNa10% (Abbreviate to HPAM). Acrylic acid (o2-acrylamide-2-methyl propane sulfonic acid) was dissolved in distilled water, and titrated with sodium hydroxide aqueous solution until the pH value was equal to 7. Acrylamide (acrylamide and sodium acrylic acid at a molar ratio of 9:1) was then added to the solution to comprise a 10% (w/w) monomer solution. The monomer solution was then poured into a four-necked flask, which was then filled with nitrogen. The aqueous ammonium persulfate and sodium bisulfite aqueous solution was then dripped through two constant pressure funnels as a redox

Figure 1. Structures of four acrylamide copolymers (a) PAM; (b) HPAMNa10%; (c) AM/AMPSNa; (d) AM/DMDAAC.
initiation. The system was maintained at 40 °C in a water bath for 8 h, and the resultant samples were stored for use.

(3) AM/AMPSNa (abbreviated to AM/AMPS). 2-acrylamide-2-methyl propane sulfonic acid was dissolved in distilled water, and titrated with sodium hydroxide aqueous solution until the pH value was equal to 7. Acrylamide (acrylamide and sodium proparesulfonic acid at a molar ratio of 9:1) was then added to the solution to comprise a 10% (w/w) monomer solution. The monomer solution was then poured into a four-necked flask, which was then filled with nitrogen. The aqueous ammonium persulfate and sodium bisulfite aqueous solutions were then dripped through two constant pressure funnels as a redox initiation. The system was maintained in a water bath at 40 °C for 8 h, and the resultant samples were stored for use.

(4) AM/DMDAAC. Next, acrylamide and dimethyl diallyl ammonium chloride (acrylamide and dimethyl diallyl ammonium chloride at a molar ratio of 9:1) was added to the solution to comprise a 10% (w/w) monomer solution. The monomer solution was then poured into a four-necked flask, which was then filled with nitrogen. The aqueous ammonium persulfate and sodium bisulfite aqueous solutions were then dripped through two constant pressure funnels as a redox initiation. The system was maintained in a water bath at 40 °C for 8 h, and the resultant samples were stored for use.

The polymerization product was mixed with excess ethanol, so that the polymer precipitated from the original aqueous solution. The mixtures were then exposed to suction filtration before being placed in a vacuum oven and dried to a constant weight. The dry solids were then crushed, re-washed with ethanol and suction filtered three additional times. Unreacted monomers and water were then completely removed from the product. Samples were replaced in the vacuum oven and dried to a constant weight. The polymer was then crushed into powder, which was sieved out using 20 mesh to 80 mesh. Finally, the product was placed into a tightly sealed sample bag, which was protected from light and maintained in a dry place until use.

2.3. Purification methods for polymer gels

The polymerization product was mixed with excess ethanol, so that the polymer precipitated from the original aqueous solution. The mixtures were then exposed to suction filtration before being placed in a vacuum oven and dried to a constant weight. The dry solids were then crushed, re-washed with ethanol and suction filtered three additional times. Unreacted monomers and water were then completely removed from the product. Samples were replaced in the vacuum oven and dried to a constant weight. The polymer was then crushed into powder, which was sieved out using 20 mesh to 80 mesh. Finally, the product was placed into a tightly sealed sample bag, which was protected from light and maintained in a dry place until use.

2.4. Polymers concentration-viscosity determination method

Determination of the viscosity temperature curve of the polymer solution was based on the corresponding polymer viscosities, and provided a solution to polymer samples in identical viscosity ranges for use in the acid resistance tests of polymer-water solutions. Successively, a certain quantity of polymer powder was weighed by analytical balance, and added gradually to an aqueous solution while stirring. When the polymer was completely dissolved, different mass concentrations were prepared with a Brookfield viscometer DV-2t. The polymer viscosity and concentration curves are shown in Fig. 3.

2.5. Polymer-acid reaction methods

2.5.1. Acid type and concentration

AR grade hydrochloric acid (36 wt%~37 wt%) was added dropwise to the polymer aqueous solutions to compose hydrochloric acid of 1 wt% and 10 wt%, respectively.

2.5.2. Degradation situation

It is generally known that acrylamide based polymers will degrade by oxidative, thermal and photodynamic effects.
Additionally, the stability of divalent ions will reduce in aqueous solutions [37–44].

In order to study the degradation of polymers in acid, the selected degradation temperature was room temperature, the polymer solutions were stored in a cool, dark, and dry place and the beakers were sealed with plastic wrap to isolate their contents from air and dust.

2.5.3. Determination of macroscopic changes in polymer aqueous solutions

In order to observe the stability of acrylamide-based polymers in acid, the above four types of prepared polymers were assembled into eight polymer solutions (two replications of each polymer type), with viscosity ranging from 10 to 30 cp. Hydrochloric acid was then added to the eight polymer solutions to comprise 1 wt% HCl and 10 wt% HCl solutions for each polymer solution. The polymer solutions were photographed and changes were recorded (Fig. 4).

2.5.4. Determination of microscopic changes in polymer aqueous solutions

In order to better observe the polymer chain microstructure by scanning electron microscopy, all mass concentrations of the polymer solutions were prepared to 1 wt%.

With mass concentrations of 1 wt%, the above four types of polymer preparations were assembled into eight polymer solutions, with two replications of each polymer. Hydrochloric acid was then added to the eight polymer solutions to comprise 1 wt% HCl and 10 wt% HCl solutions for each polymer solution. After one hour, the microstructure of the polymer samples was observed by scanning electron microscopy (Fig. 5).

2.5.5. Determination of changes in apparent viscosity

Hydrochloric acid was added dropwise into polymer solutions of specific viscosities to comprise mass fractions of hydrochloric acid equal to 1 wt% and 10 wt%. Fig. 6 depicts the apparent viscosity of the polymer aqueous solution after the addition of HCl (time zero indicates no acid addition). Fig. 7 depicts the viscosity decrease range of the eight polymer solutions based on the results presented in Fig. 6.

2.5.6. Determination of changes in polymer molecular weight change

After acid was dripped into the polymer solutions, the solution viscosity declined to a great extent. The effect of the polymer chains on the decreased viscosity was analyzed by assessing changes in the polymer chain distribution. Additionally, changes in molecular weight were measured by ubbelohde viscometry.

The steps are as follows. First, four types of aqueous polymer solutions were prepared to achieve 1 wt%; each polymer aqueous solution was produced in seven replicates. Secondly, hydrochloric acid was dripped into the four types of polymer solutions to achieve acid mass fractions of 1 wt% and 10 wt%, respectively. Thirdly, ethanol was added to the samples in order to purify them after acid soaking times of 1 h, 10 h, and 100 h, respectively. Next, according to the China national standard GB-T12005.1–89, the dilution method was applied in order to determine the intrinsic viscosity of polyacrylamide in the polymer solutions, and the acrylamide polymer molecular weight of degradation was calculated at 0 h (i.e., without the addition of acid), 1 h, 10 h, and 100 h. The results are depicted in Figs. 8, 9.

3. Results and discussion

3.1. Polymer concentration-viscosity curves

As shown in Fig. 3, the thickening ability of the four polymers varied greatly. The initial viscosity (0.1 wt%) was observed according to the following inequality: AM/AMPS > HPAM > PAM > AM/DMDAAC. As the mass fraction of HCl increases, the relationship between the concentrations of the four polymers and their respective apparent viscosities is approximately linear. The four types of polymers demonstrate increasing viscosity according to the following relation: HPAM > AM/AMPS > PAM >
AM/DMDAAC. The initial viscosity (0.1 wt%) is described as follows: AM/AMPS > HPAM > PAM > AM/DMDAAC. The viscosities of the two polymers (HPAM, AM/AMPS) which contained anions (carboxylic acid, sulfonic group) are significantly greater than that of PAM and AM/DMDAAC.

### 3.2. Macroscopic changes of polymer aqueous solution in acid

As shown in Fig. 4, the degradation phenomena of the four acrylamide-based polymers in 1 wt% HCl and 10 wt% HCl demonstrated significant differences. The four polymer aqueous solutions in 1 wt% hydrochloric acid remained clear and transparent after 30 days (Fig. 4a, c, e, g). However, the four polymer solutions in 10 wt% hydrochloric acid varied greatly. Based on the changes exhibited by the four polymer solutions, immediate stability was fairly strong. However, after 30 days, the four polymer solutions demonstrated significant changes. Among them, the AM/AMPS solution exhibited no obvious change (Fig. 4f), while PAM (Fig. 4b) and HPAM (Fig. 4d) exhibited precipitations on the bottom of their respective beakers and AM/DMDAAC demonstrated an emulsifying phenomenon (Fig. 4h).

In conclusion, some of the studied polymers exhibited a precipitation phenomenon which directly indicated partial polymer degradation induced by high concentrations of liquid acid. As time progressed, the degradation phenomena varied significantly, indicating that the acid concentration and methods of polymer modification directly influenced the stability of the polymer in acid. Finally, the three polymers modified by anionic and cationic monomers exhibited greater stability in acid than PAM, thus proving that increasing polymer charge ability contributes to the increased stability of polymers in acid. The four polymer solutions were relatively stable in 1 wt% hydrochloric acid solution, but demonstrated poor stability after long exposure to 10 wt% hydrochloric acid solution, with the exception of AM/AMPS. Thus, the stability of the four polymers in hydrochloric acid was observed according to the following relation: AM-AMPS > HPAM > AM/DMDAAC > PAM.

### 3.3. Microscopic changes to polymer aqueous solution in acid

As shown in Fig. 5, before the addition of hydrochloric acid, a clear network structure was observed in the four polymer chains. The distance between the four polymers of the charged groups was relatively uniform and their primary chain structures were clear. The morphologies of the four acrylamide-based polymers were significantly different in water solutions. PAM polymer chains were relatively uniform in their dispersion, and an aggregation phenomenon was observed which formed ribbon-like polymer chains (Fig. 5a). HPAM exhibited a uniform distance between chains and the primary chain was distributed directionally (Fig. 5d). AM/AMPS polymer chains aggregated significantly.
apparently (Fig. 5g). The AM/DMDAAC polymer chains exhibited 
parallel arrangements, and chains contained some ball-linked 
chains (Fig. 5j).

After the addition of hydrochloric acid, the eight polymer 
chains began to shrink, and the polymer network structure 
gradually disappeared. Among the solutions, PAM demonstrated 
a slug (flake) structure (Fig. 5b, c), HPAM demonstrated a chain 
scission phenomenon (Fig. 5d, e, f), AM/DMDAAC demonstrated 
significant damage to the polymer network structure (Fig. 5d, k, l) 
and AM/AMPS polymer chains began to gather and contract 
(Fig. 5d, h, i). Results indicate significant microstructural 
changes, which were exacerbated by the addition of high-
concentration acid.

Based on the observed macroscopic and microscopic changes, 
it was concluded that the addition of acid to polymer solution 
results in the following alterations.

In PAM solutions, the hydrogen ions combine with amide 
group resulting in positively-charged polymer chains. PAM 
therefore exhibits some acid resistance as a result of the effects of 
electrostatic repulsion. However, in 10 wt% HCl solutions, the 
high hydrogen ion concentration resulted in the sudden satu-
ration of amide groups. This caused the polymers in 10 wt% HCl 
to gather, shrink and degrade, finally resulting in the formation 
of a precipitate in the bottom of solution beakers after 30 days 
(Fig. 4d). In HPAM solutions, before the addition of acid, the 
carboxyl group of the polymer chains exhibited electrostatic 
repulsion, maintaining the distance between chains and result-
ing in the directional distribution of the primary chains. Upon 
the addition of acid, the carboxyl groups in HPAM first combined 
with hydrogen atoms so that the polymer chains would be less 
affected by the addition of acid. In AM/AMPS solutions, the 
charge of the sulfonic group is stronger than that of the carboxyl 
group, so that the effects of electrostatic repulsion are greater 
than in HPAM solutions. To some extent, the strong charge 
provides better stability in acid solutions. In AM/DMDAAC solu-
tions, the positive charge of the quaternary ammonium groups 
provided some resistance to hydrogen ions as a result of elec-
 trostatic interactions. However, this charge is weaker than that in 
AM/AMPS, resulting in severe damage to the network structure.

The emulsion phenomenon (Fig. 4p) indicates the cleavage of 
some polymer chains, which produced substances with surfac-
tant properties.

### 3.4. Change in apparent viscosity

As shown in Fig. 6, when acid was added dropwise into the 
eight polymer solutions, their viscosities were quickly 
reduced within ten hours, but after ten hours the reduction 
speed decreased significantly. The viscosity decline was observed 
according to the following relation: HPAM > AM/AMPS > PAM > 
AM/DMDAAC.

For aqueous solutions of the same polymer, the viscosity of 
1 wt% HCl polymer solution was greater than that of 10 wt% 
HCl polymer solution. The relation of viscosity difference 
observed from the same polymer between 1 wt% HCl polymer 
solution and 10 wt% HCl polymer solution was observed 
according to the following relation: PAM > AM/AMPS > HPAM > 
AM/DMDAAC.

The changes observed in the viscosities of the four types of 
polymer solution varied significantly. Among the observed 
changes, HPAM was nearly 70%, AM/AMPS was nearly 60%, AM/

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**Figure 6.** Polymer aqueous solution apparent viscosity changes after the addition of acid. (a) 2 wt% PAM; (b) 1 wt% HPAM; (c) 0.4 wt% AM/AMPS; (d) 2 wt% AM/DMDAAC.

**Figure 7.** The decrease of apparent viscosity of polymer solutions after addition of acid (100 h).
DMDAAC was nearly 34%, and PAM was nearly 20%. After the addition of acid, changes in the viscosity in the four types of polymer solution after 100 h included the following: 0.4 wt% AM/AMPS was 7.7 cp (10 wt% HCl), which exceed the value exhibited by 1 wt% PAM in 10 wt% HCl. Therefore, the thickening performance of AM/AMPS in high-concentration acid solution was relatively good.

A comparison of the thickening performances of the four polymer types and their ability to maintain viscosity in acid indicates that polymers which thickened faster also exhibited more rapid reduction of viscosity. This indicates that the addition of acid may result in severe damage to electrostatic interactions between polymer chains and lead to changes in hydrodynamic characteristics. This is the reason behind the changing viscosities of the polymer solutions.

A comparison of Fig. 6b and c indicates that the viscosity reduction percentages were nearly identical, and that after the addition of acid, the viscosity of AM/AMPS decreased at a slower rate. This may be because the CO−NH bond in the acid induced hydrolytic cleavage and the hydrolysis product of AM/AMPS was similar to that of HPAM. A comparison of Fig. 6a and d indicated that the two mass fractions of 2 wt% polymer solution exhibited relatively small decreases in viscosity over time. The 2 wt% PAM solution in 1 wt% HCl demonstrated a slower rate of viscosity decrease and a smaller range than that of the 10% HCl solution. The 2 wt% AM/DMDAAC polymer solution exhibited nearly identical viscosity decreases and ranges for both the 1 wt% HCl and the 10 wt% HCl solutions. Results indicate that high concentrations of hydrochloric acid have great influence on PAM, while the impact on AM/DMDAAC is relatively small.

3.5. Change in polymer molecular weight

At identical time increments, for the identical polymer, polymer molecular weight observed from the 1 wt% HCl polymer solution is greater than that observed from the 10 wt% HCl polymer solution.

As demonstrated above, when acid was dripped into the eight polymer solutions, the polymer molecular weight declined according to the following relation: HPAM > AM/AMPS > PAM > AM-DMDAAC. The viscosity relationship between 1% HCl polymer solution and 10% HCl polymer solution derived from identical polymers declined according to the following relation: PAM > AM-AMPS > HPAM > AM-DMDAAC.

The changes in polymer weight indicated that high concentrations of hydrochloric acid results in the direct fracture of the polymer backbone. Additionally, speeds of polymer degradation vary significantly, indicating that the modification of polyacrylamide with functional monomers is meaningful.
As reported by Muller et al., polyacrylamides undergo hydrolysis under acidic conditions to yield poly(acrylamide-co-acrylic acid). Amide groups will completely hydrolyze under conditions of appropriately low pH, and polymer weight will remain relatively stable during hydrolysis, as the following formula [17–19]. Compared to their studies, the present study determined that the molecular weight of PAM was relatively stable after the dropwise addition of 1 wt% HCl after 1 h. As time progressed, the extreme acidic conditions induced hydrolysis of the amide groups to form carboxylic acid groups. The polymer chains then began to scission so that the polymer weight was gradually reduced. The phenomenon exhibited by the PAM sample in 10 wt% HCl was much more clearly observed.

The difference observed between the hydrolysis of HPAM and PAM was that PAM hydrolyzed at a slower rate, resulting in the faster degradation of HPAM. Comparing AM-AMPS to HPAM, the CeN bond in AM-AMPS underwent acidic hydrolysis. Thus, the changes in the apparent viscosity and the molecular weight of HPAM were relatively similar to those of AM-AMPS, and AM-AMPS degraded at a slower rate than HPAM.

Alternative to the results demonstrated by PAM, AM-DMDAAC was modified by allyl ammonium chloride, resulting in positively-charged polymer chains. Due to the effect of electrostatic repulsion, the polymer chains in AM-DMDAAC become more resistant to hydrogen ions at an early stage. As more amide groups in AM-DMDAAC hydrolyze to carboxylic acid groups, gradual degradation also occurs. Emulsion occurs as a result of the product generated by the degradation product and the surface active, as shown in Fig. 4h.

4. Conclusions

In this work, the stability of different modified acrylamide-based polymers in high concentrations of hydrochloric acid was comprehensively investigated. The primary contributions of the present study are described as follows.

(1) The response of acrylamide polymers in the pH range and in greater than 1 wt% hydrochloric acid exhibits significant differences when applied to different polymer solutions. Based on the observation of macroscopic changes to different modified acrylamide polymer aqueous solutions in different concentrations of acid, the exhibited phenomena varied greatly. Results indicate that 10 wt% HCl damages the polymer stability in aqueous solutions after 30 days; however, polymer solutions with 1 wt% HCl were relatively stable after the same amount of time. This indicates that applied acrylamide-based polymers should take into account the acid concentration in order to effectively modify the polymer.

(2) A possible mechanism describing the effect of hydrogen ions on polymer chain structures and precipitation is proposed. Observation of microscopic changes in polymer chain structure by SEM in 1 wt% HCl and 10 wt% HCl indicate that 10 wt% HCl demonstrated the greatest effect on the polymer chains. The high concentration of hydrogen ions damages the network of most acrylamide-based polymers and causes the polymer chain to gather and shrink, resulting in decreased water solubility.

(3) Acid may severely damage the electrostatic interactions between polymer chains and lead to changes in the hydrodynamic characteristics of the polymer. Changes to the apparent viscosity of polymers were investigated in identical acid concentrations. The results indicate that polymers which thickened faster also exhibit more rapid reductions of viscosity. Of the studied solutions, AM-AMPS exhibited the best viscosity maintenance in 10 wt% HCl.

(4) The changes in polymer molecular weight indicate that the high concentrations of hydrochloric acid gradually degraded the four acrylamide-based polymers, demon-

strating that the modification will have significant effect on their acid resistance.

(5) The comprehensive understanding of the effects of high concentration acid solutions on acrylamide-based polymers has important significance for stability maintenance, and the present study provides guidance for polymer modification and applications.

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