

Article

Synthesis and Mechanism Study of Temperature- and Salt-Resistant Amphoteric Polyacrylamide with MAPTAC and DTAB as Monomers

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Abstract: The failure of thickeners at high temperature results in gelled acid acidification fracturing. To solve the problem, 8 kinds of polymers were synthesized by free radical polymerization of aqueous solution using AM, AMPS, NaAMPS, MAPTAC, DTAB and NVP as raw materials. The polymer was characterized by infrared spectroscopy and viscosity-average molecular weight, and the temperature resistance, rheology, salt resistance and shear resistance of the polymer solution were compared, and the mechanism was analyzed. The results show that the viscosity of GTY-2 is 181.52 mPa·s, and the viscosity loss rate is 56.89% at 180 °C and 100 s⁻¹, and its temperature resistance is the best. Meanwhile, the viscosity retention rate of GTY-2 is 84.58% after 160 min shear, showing the strongest shear resistance. The viscosity loss rate of GTY-1 in 20% hydrochloric acid solution is 80.88%, and its acid resistance is stronger than that of GTY-2. Moreover, due to the amphiphilicity of DTAB, the molecular hydration film becomes thicker, and the salt resistance of GTY-2 is lower than that of GTY-1. The experimental results show that GTY-1 and GTY-2 have good temperature resistance, salt resistance, acid resistance and shear resistance, and can be used as thickeners for acid fracturing with thickened acid to improve the effect of acid fracturing under high temperature conditions.

Keywords: acid fracturing; polyacrylamide; thickener; high temperature resistance; viscosity loss rate



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1. Introduction

Currently, more than 60% of oil reserves and 40% of natural gas reserves come from carbonate reservoirs [1]. Carbonate oil and gas reservoirs have poor matrix permeability and low porosity [2], but they have well-developed natural fractures and caves, of which limestone caves and fractures are the main reservoir and seepage space [3]. However, the distribution pattern of natural fractures and limestone caves is uncertain and uneven, and the connectivity is generally poor [4]. Previous development practices of carbonate reservoirs have proved that acid fracturing can effectively connect natural fractures with limestone caves. Whether near the wellbore or in the far well zone, it is an important technical means to improve the production of such reservoirs [5]. In addition, as a technology to enhance oil recovery, acid fracturing can effectively relieve the formation permeability reduction as well as the blockage caused by pollution in the near-well zone. This technology significantly improves the permeability of reservoirs and increases crude oil recovery [6].

However, the acid rock reaction rate determines the success or failure of the whole acid fracturing work. Therefore, a variety of acid fluid systems have been developed to control the speed of acid rock reaction, such as thickened acid [7]. On the one hand, thickened acid can reduce the filtration of acid solution; on the other hand, it can form a colloidal network structure and reduce the diffusion of H⁺ [8]. In addition, the thickened acid also

has the characteristics of forming wide fractures during acid fracturing, with low friction [9] and good performance of suspended solid particles [10], so it is widely used in carbonate reservoir reconstruction.

The thickened acid system includes a thickener, corrosion inhibitor, iron ion stabilizer and other additives [11]. With the development of carbonate oil and a gas reservoir to the field of high temperature and deep well, the existing thickener molecules have chain fracture at high temperature, the molecular long chain becomes shorter, the molecular weight decreases, the viscosity increasing effect becomes worse, and the viscosity of the acid system decreases significantly, which increases the diffusion rate of H^+ and speeds up the acid rock reaction. Therefore, a large amount of fresh acid is consumed near the well, which is difficult to penetrate the reservoir in depth, and the fracture conductivity is low [12]. However, the current oil industry rarely develops thickeners with high temperature resistance. Therefore, the development of a high-temperature-resistant thickener is of great significance for the development of a carbonate reservoir under high temperature. In addition, large-scale fracturing technology is often used in the development of unconventional oil and gas reservoirs, especially in shale oil. A large number of carbonate minerals contained in shale oil reservoirs are the main components of bedding and schistosity in shale reservoirs. Therefore, the research and development of a high-temperature-resistant thickener can also provide technical reserves for the development of shale oil reservoirs [13].

Acrylamide polymer is one of the main types of acid thickeners, which has been studied by many scholars. The Larry Eoff [14] research team proposed for the first time to shift the acidification of hydrophobically associating polymers to carbonate reservoirs. The field application of hydrophobically modified polyacrylamide and dimethylaminoethyl methacrylate shows that the hydrophobically associating polymer not only has good conductivity effect, but also the water production rate is reduced from 21% to 17%. It solves the problem of water output after formation acidification and presents good application advantages. However, they only evaluated the conductivity effect and did not study the viscosity change process of hydrophobically associating polymers in acid rock reaction. Jin et al. [15] studied the mechanism of shear induced self-thickening of chitosan-grafted polyacrylamide aqueous solution around the shear effect, and pointed out that the intermolecular hydrogen bond plays a leading role in the aggregation effect. Unfortunately, the research was only carried out below 50 °C and the temperature is low. In contrast, Gou et al. [16] studied the thickening, shear stability and salt resistance of the new acrylamide-based copolymer prepared by acrylic acid, sulfonate and acrylamide in the range of 80–110 °C, and the research temperature increased slightly, but only studied the temperature resistance of thickener aqueous solutions, and did not further study its high temperature resistance and acid resistance stability. Similarly, Qi Wu [17] studied the characteristics of temperature and salt resistance, shear resistance and thickening with hyperbranched polymer. He did not consistently study the stability of acid resistance and higher temperature. Haiyang Tian [18] and others synthesized a new betaine-type hydrophobically associating polyacrylamide and evaluated its acid resistance. Insufficiently, they only studied the temperature stability in the range of 25–120 °C, and did not study the high temperature resistance above 140 °C. In the high temperature field above 140 °C, Chen et al. [19] prepared hydrophobically associating polyacrylamide (HACA) using AM, AMPS, DMC and NVP. The retention viscosity of 0.4% HACA after shearing for 2 h at 150 °C and 170 s^{-1} is 99 mPa·s. The system has good thickening ability and temperature resistance. Zhang et al. [20] copolymerized acrylamide, 2-acrylamide-2-methylpropanesulfonic acid and acryloylmorpholine, and introduced polyvinyl alcohol fiber to synthesize a new polyacrylamide copolymer. The modified polymer has good salt resistance and still has a viscosity of 72.74 mPa·s at 150 °C and 170 s^{-1} . However, the product synthesized by Chen and Zhang is only used as a fracturing thickener, and its acid resistance has not been studied to prove whether it can be used for acid fracturing. In the ultra-high temperature field above 180 °C, Prakash C. [21] and others synthesized a ternary polymer and crosslinked it with organic zirconium. The sys-

tem was sheared for 2 h at 200 °C and 40 s⁻¹, and the viscosity remained above 500 mPa·s. The shear resistance of the polymer was not studied under the shear rate of 170 s⁻¹.

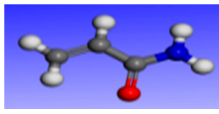
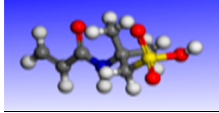
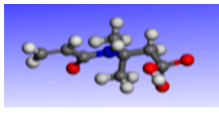
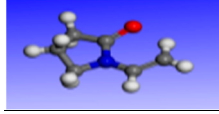
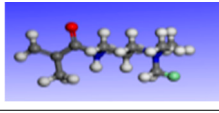
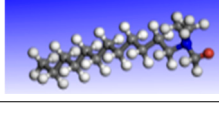
The previous research mainly reflected the following research gaps: (1) the research on the temperature resistance of polyacrylamide acid thickener is not deep enough, and it is difficult to involve the ultra-high temperature field above 180 °C; (2) the research on the acid resistance stability of acid thickeners is not specific, and there is no research on the acid resistance mechanism; (3) as a thickener, polyacrylamide mainly focuses on hydraulic fracturing, and does not involve the application of carbonate acid fracturing. Based on this research background, a series of binary, ternary and quaternary copolymers with diluted amide, 2-acrylamido-2-methyl-1-propane sulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid sodium salt, N-vinyl pyrrolidone, methacrylamide oxyethyl trimethylammonium chloride and dodecyl trimethylammonium bromide as reactants were synthesized in this paper. The structure of the synthesized polymer was characterized and analyzed by NMR and a tunneling scanning microscope, and the reaction mechanism was obtained. Secondly, according to the viscosity experiment, we evaluated the temperature and acid resistance of the synthetic polymer, and analyzed its temperature and acid resistance mechanism according to the structure of the polymer. Finally, according to the rheological experimental results, the shear capacity of the polymer is evaluated and its mechanism is analyzed. According to the experimental process and results of this paper, a new high-temperature-resistant thickening acid fracturing thickener is proposed, which provides a theoretical basis and technical innovation for the research of the high temperature field of acid fracturing technology.

2. Methodology

2.1. Materials

The monomers used in the experiment are shown in Table 1.

Table 1. The monomers used in the experiment.

Bat Model	Name	CAS	Specifications (%)	Packing	Target
	(AM) Acrylamide	76-06-1	AR	500 g	Molecular chain
	(AMPS) 2-Acrylamide-2-Methylpropanesulfonic Acid	15214-89-8	98	100 g	Temperature and salt resistance
	(NaAMPS) Sodium 2-Acrylamide-2-Methylpropanesulfonate	5165-97-9	50 wt	25 mL	Temperature and salt resistance
	(NVP) N-Vinylpyrrolidone	88-12-0	99	100 mL	Temperature resistance
	(MAPTAC) Methacrylamide propyl Trimethyl Ammonium Chloride	51410-72-1	50 wt	100 mL	Temperature resistance
	(DTAB) Dodecyl Trimethyl Ammonium Bromide	1119-94-4	99	100 g	Temperature resistance
	(K ₂ S ₂ O ₈) Potassium Persulfate	7727-21-1	99.5	100 g	Initiator

The above chemical reagents have been purified and can be used directly. MAPTAC was purchased from Beijing Datian Fengtuo Chemical Technology Co., Ltd., Beijing, China, and the other reagents were purchased from Shanghai McLean Biochemical Technology Co., Ltd., Shanghai, China. The monovalent and divalent inorganic salt ions such as NaOH, NaCl, CaCl₂, and MgCl₂ used in the study are analytical pure reagents, which were directly used and purchased from the Tianjin Yongda Chemical Reagent Factory, China.

2.2. Experimental Setup and Procedure

2.2.1. Synthesis and Characterization of Thickener

(1) Preparation of copolymerization solution: accurately weigh a certain amount of AM, AMPS, NaAMPS, DTAB, NVP and MAPTAC monomers according to the proportion in Table 1, add them into deionized water for mixing, and fully stir to obtain binary, ternary and quaternary reactant mixed solutions.

(2) Add an appropriate amount of 40% NaOH solution and adjust the pH value of the solution to pH = 6.

(3) Add the mixed solution into a three-neck flask and place it in a constant temperature water bath pot with the set temperature of 40 °C.

(4) Adjust the agitator, set the speed to 300–350 r/min, and continuously supply nitrogen for 30 min to ensure the continuity and uniformity of bubbles, and stir for deaeration.

(5) Set the temperature to 60 °C, add the initiator K₂S₂O₈ to the reaction vessel, seal the mouth of the flask, and adjust the stirring speed to 100–150 r/min and react 12 h after the temperature rises to 60 °C.

(6) Pour the mixed solution into absolute ethanol, filter and remove the ethanol, dry it in a vacuum under 50 °C oven for 12 h, and crush it with a granulator to obtain solid powders of various binary, ternary and quaternary copolymers.

(7) After drying the KBr powder, take three spoons and put them into a mortar, then add a small amount of solid powder, grind them to make them evenly mixed, press them with a press, and scan them in Spectrum one FT-IR spectrometer. In addition, take a small amount of solid powder and scan it in the scanning electron microscope.

2.2.2. Determination of Viscosity Average Molecular Weight M_w

Compared with M_n , M_w takes into account the contribution of the single-chain molecular weight to the molecular weight when determining the average molecular weight. For the viscosity of polyacrylamide at high temperature, the viscosity of the polymer solution is affected by the size of the single-chain molecular weight. Therefore, the molecular weight of the synthesized polyacrylamide was characterized by measuring MW by a Ubbelohde viscometer. The instrument used in the experiment is a Ubbelohde viscometer, as shown in Figure 1.



Figure 1. Ubbelohde viscometer. A—Air suspension pipe; B—Measuring capillary; C—Liquid injection pipe; D—Round pipe; E—Quantitative sphere; F—Liquid ball; G—Buffer ball; a—Upper score line; b—Lower score line.

(1) Draw 15 mL of prepared 1000 mg/L polymer solution with a pipette, inject it from viscometer tube A, and keep the temperature at 30.05 °C for 5 min.

(2) After constant temperature for 5 min, press tube C by hand, put the ear ball at the mouth of tube B, suck the solution to ball G, and then release it.

(3) When the solution drops to line a, press the stopwatch to record the time. When the solution drops to line b, press the stopwatch to end the experiment, noting t . Repeat the measurement three times, and the time difference between each two times shall not exceed 0.2 s.

(4) After measuring the polymer solution with the concentration of 1000 mg/L, use a pipette to suck 1 mol/L of NaCl solution in the volumetric flask in the constant temperature bath, add it from tube a, press and hold tube C, and use a suction ear ball to repeatedly press and suck the solution from the orifice of tube B to make the mixture uniform. The determination method is shown in (3), noting t_0 .

(5) Add 2 mL, 2 mL and 4 mL of 1 mol/L NaCl solution successively, and measure according to steps (4).

(6) Calculate the relative viscosity of the sample solution according to Formula (1):

$$\eta_r = \frac{t}{t_0} \quad (1)$$

where: η_r —relative viscosity;

t —flow time of the sample solution, s;

t_0 —flow time of 1.00 mol/L of the sodium chloride solution, s.

Find the corresponding $[\eta]$ ·C value from the obtained η_r , and divide the $[\eta]$ ·C value by the sample concentration C to obtain $[\eta]$.

(7) The molecular weight is calculated according to Formula (2) [22]:

$$[\eta] = KM^\alpha \quad (2)$$

where: M —average value of the relative molecular weight of polymer;

K —proportional constant, $K = 3.34 \times 10^{-4}$ [23];

α —empirical parameters related to the morphology of polymers in solution, $\alpha = 0.708$ [23].

2.2.3. Rheological Test and Viscosity Test of Thickener Aqueous Solution

(1) Add polymer solid powder into distilled water at 60 °C, prepare 10 g/L of polymer solution, and seal with fresh-keeping film.

(2) Replace the heating liquid of the rheometer, start the rheometer, calibrate and preheat it to 120 °C.

(3) Remove the protective film, drop a few drops of polymer solution onto the rheometer test bench, and test the viscosity of the polymer at a shear rate of 0–100 s⁻¹.

(4) Set the experimental temperature to 135 °C, 150 °C, 165 °C and 180 °C, and repeat the experimental steps of (2)–(4).

(5) Take an appropriate amount of polymer powder and 36% hydrochloric acid solution or different types of salt (Ca²⁺, Mg²⁺, Na⁺) solution to prepare 10 g/L of polymer solution. The acid concentration is 0, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 1%, 2%, 3%, 4%, 5%, 10%, 15% and 20%, respectively. Inorganic salt concentration is between 400 and 3200 mg/L.

(6) Select the acid-resistant rotor, start the rheometer for calibration, and measure its viscosity at 25 °C and 170 s⁻¹.

(7) Prepare 10 g/L of polymer solution, and test the viscosity of the polymer solution under the condition of 170 s⁻¹ after shearing at 25 °C and 3500 r/min for 0–160 min.

3. Results and Discussion

3.1. Characterization and Mechanism of the Product

3.1.1. Synthesis Results and Characterization

In order to synthesize salt-resistant polymers with high temperature resistance, acid resistance and shear resistance, taking acrylamide as the main chain and some monomers with rigid chain structure with high temperature resistance and acid resistance as the side chain, the corresponding polymer synthesis experiments were carried out without pursuing the yield. The experimental conditions are shown in Table 2.

Table 2. Experimental raw materials.

Number	Raw Material	Mole Proportion
1	AM, AMPS	4:1
2	AM, NaAMPS	4:1
3	AM, NaAMPS, MAPTAC	4:1:0.1
4	AM, NaAMPS, DTAB	4:1:0.1
5	AM, NaAMPS, NVP	4:1:0.1
6	AM, AMPS, DTAB	4:1:0.1
7 (GTY-1)	AM, NaAMPS, NVP, MAPTAC	4:1:0.1:0.1
8 (GTY-2)	AM, NaAMPS, NVP, DTAB	4:1:0.1:0.1
9	Commercial products (from Liaohe Oilfield Co., Ltd., Shenyang, China)	None

The results are shown in Figure 2. Figure 2b shows that the mixture solution in the three-neck flask is obviously sticky, and white insoluble matter is precipitated in ethanol (Figure 2c). The synthesized polymers are purified and ground into powder, as shown in Figure 2d. Therefore, it is inferred that the raw material did undergo polymerization. In order to verify the conjecture, the infrared spectrum experiment is carried out, and the experimental results are shown in Figure 3.

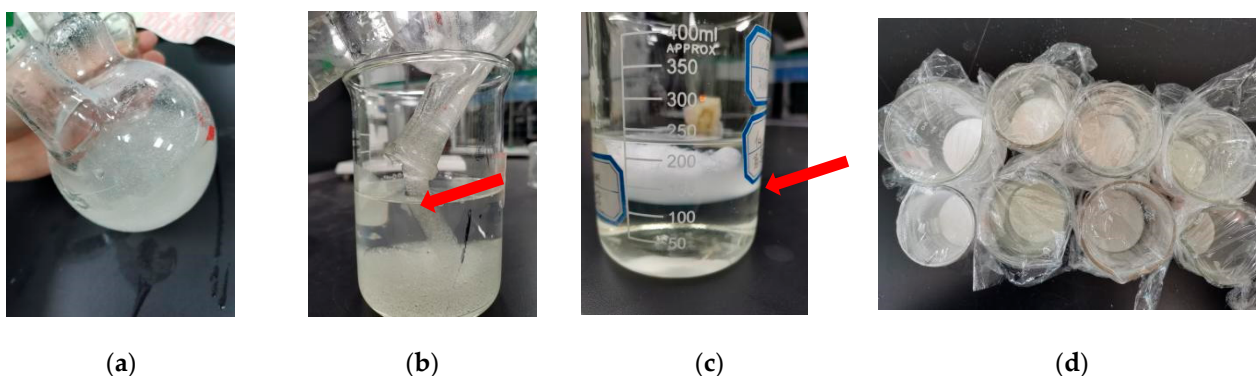


Figure 2. Schematic diagram of synthesis operation. (a) Mixture of product and reactant; (b) Mixture solution during purification; (c) Separation from ethanol; (d) Synthetic polymer ground into powder.

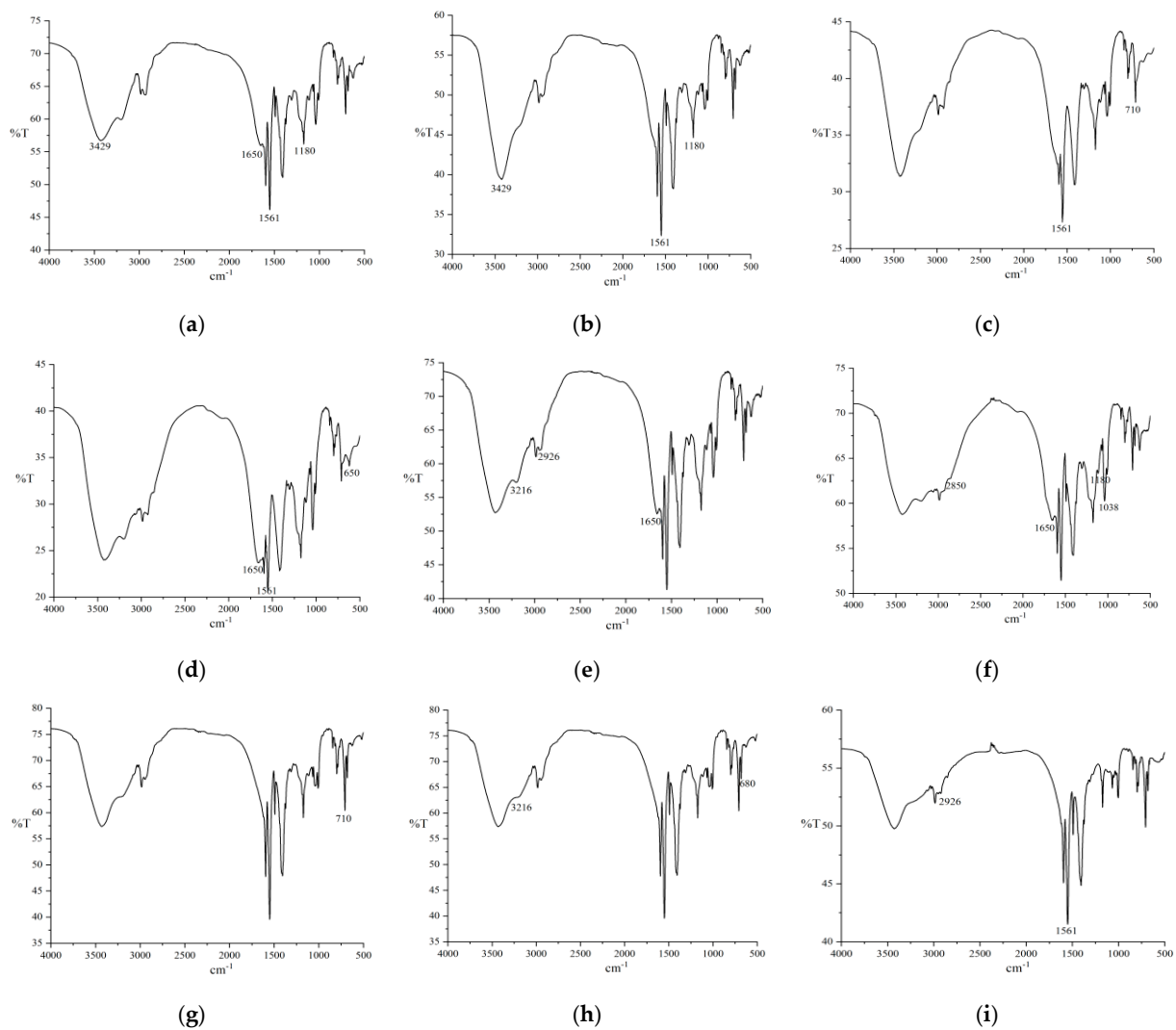


Figure 3. Infrared spectrum of synthetic polymer. (a). No. 1; (b). No. 2; (c). No. 3; (d). No. 4; (e). No. 5; (f). No. 6; (g). GTY-1 (No. 7); (h). GTY-2 (No. 8); (i). No. 9.

As can be seen from Figure 3, the infrared spectra of 9 polymers including No. 9 (Liaohe Oilfield Polymer) are basically similar. Some common absorption peaks are shown in Table 3.

Table 3. Some common absorption peaks.

Location (cm ⁻¹)	The Characteristic Absorption Peak
3429	Free -NH ₂
3216	Associated -NH ₂
2926	Methylene antisymmetric stretching vibration
2850	Methylene symmetric stretching vibration
1650	Amide group
1620	Amide II (N-H bending vibration)
1561	The bending vibration of secondary amide N-H
1453	Methylene deformation
1180	Acyloxy group
1038	Sulfonic acid group

The absorption peak at 1174 cm^{-1} is obvious in the cationic products, which is generally related to the stretching vibration of C-N. This absorption peak is obvious in the two polymerization products of polymers No. 1 and No. 2. This is because the raw materials of the synthetic polymer are AM, AMPS and NaAMPS, and do not contain monomers that can contain dissociated anions. In the synthesis of Nos. 3–8, the raw materials include chloride and bromide. Therefore, in the infrared spectrum, there are obvious absorption peaks of chloride and bromide, which are 710 cm^{-1} absorption peak and 650 cm^{-1} absorption peak, respectively. This is because chloride and bromide can ionize anions after the synthesis of polymer, neutralize with the charge generated by ionized cations, and produce anti-polyelectrolyte, which prevents the viscosity of the solution from greatly decreasing with the increase of the concentration of added salt, so as not to reduce its tackifying ability. It can be seen from the above analysis that No. 1 and No. 2 are cationic polyacrylamide, while Nos. 3–8 are amphoteric polyacrylamide and amphoteric polyelectrolyte.

Then, the molecular weight of the synthesized polymer was characterized to prepare for the subsequent performance evaluation. The results are shown in Figure 4.

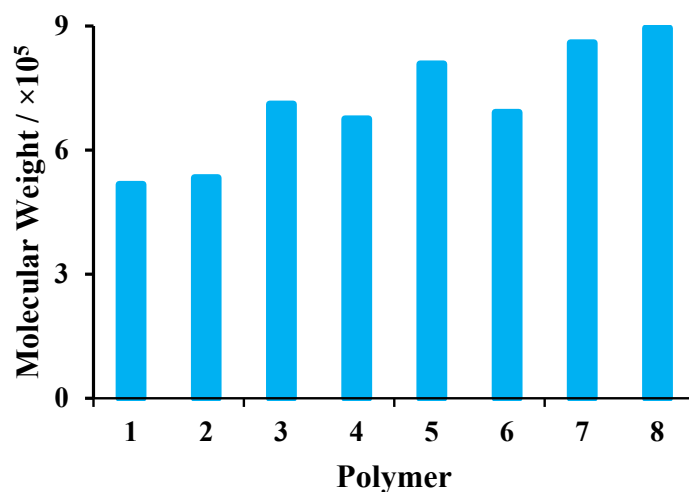


Figure 4. Intrinsic viscosity and molecular weight of the synthetic polymer.

It can be seen from the figure that the molecular weight of the polymer is between 5 and 9×10^5 . Among them, the molecular weights of GTY–1 and GTY–2 are significantly higher than those of other polymers, which are 8.59×10^5 and 8.95×10^5 , respectively, which is mainly due to the fact that they are quaternary polymers with higher reactant concentration and higher molecular weight of the resulting polymer.

3.1.2. Study on Synthesis Mechanism

From the infrared spectrum of the synthetic polymer and the molecular weight data of the polymer, it can be proven that the corresponding monomer was successfully synthesized into a macromolecular polymer through addition polymerization. The polymerization reaction is mainly through the opening of unsaturated bond—carbon–carbon double bond. For specific reaction, take No. 1, No. 2, No. 3 and GTY–1 as examples; see Figure 5.

3.2. Evaluation and Mechanism of Temperature Resistance

In order to investigate the temperature resistance of the synthetic polymer, the rheology in the temperature range of $120\sim 180\text{ }^\circ\text{C}$ was studied. The experimental results are shown in Figure 6.

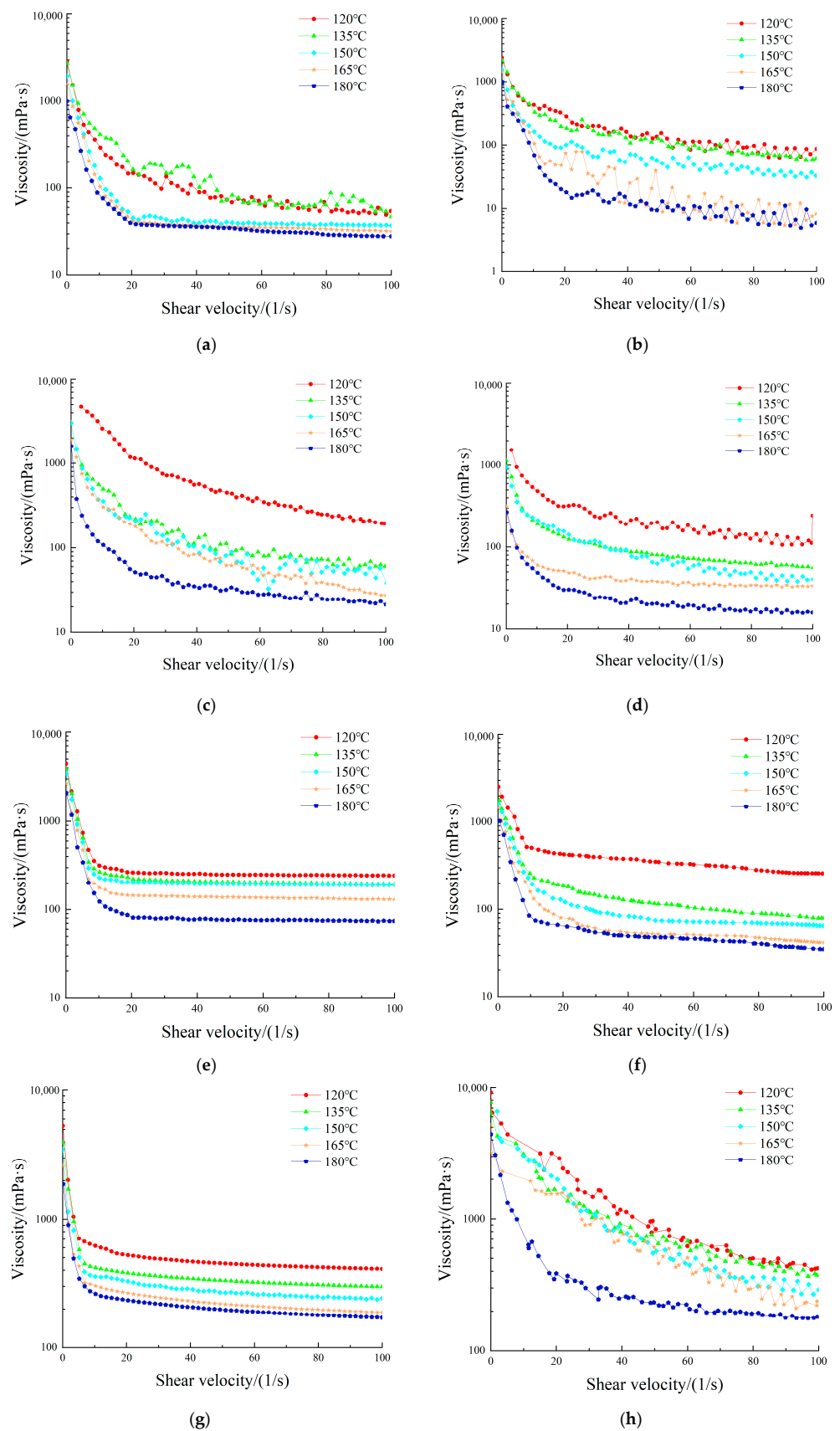


Figure 6. Test results of polymer rheology. (a) No. 1; (b) No. 2; (c) No. 3; (d) No. 4; (e) No. 5; (f) No. 6; (g) GTY-1 (No. 7); (h) GTY-2 (No. 8).

It can be seen from Figure 6 that the rheology of all polymers decreases with the increase of shear rate, showing the characteristics of shear dilution. The viscosity decreases with the increase of temperature. In addition to the degradation of polymer at high temperature, the increase of temperature will change the diffusion capacity of water molecules, increase the rotation energy within the molecules, make the coil more curly, and enhance the polarity of water, which is similar to the compression of electric double layers by electrolytes [18], making the hydration film of the macromolecular coil thinner, and the mechanical volume of fluid smaller, which is macroscopically shown as the viscosity reduction.

Figure 6g,h shows that under the condition of 180 °C and 100 s⁻¹, the viscosity of GTY-1 is the largest, which is 181.52 mPa·s, followed by GTY-1, which is 170.73 mPa·s, which is significantly higher than other polymers. The viscosity loss rate of GTY-2 is 56.89%, and that of GTY-1 is 58.26%, which is significantly lower than that of other polymers, as is shown in Table 4. Therefore, it can be concluded that GTY-2 has the best temperature resistance, followed by GTY-1, and is significantly better than other polymers.

Table 4. Viscosity Loss in temperature of 180 °C.

Polymer	Viscosity (mPa·s)	Loss Rate (%)
GTY-1	181.52	58.26
GTY-2	170.73	56.89

The reasons for the difference in temperature resistance of polymers are analyzed as follows:

1. Hydrogen bonding [24]. There are N atoms and O atoms with large electronegativity in NaAMPS, NVP and DTAB introduced by polymer molecules, which form hydrogen bonds with H atoms in the system, thus increasing the viscoelasticity of polymer solutions.
2. The strong electrostatic repulsion (anion) effect of the added -SO₃ ion group makes the sulfonate polymer have high hydration ability, which can enhance the steric hindrance of the polymer straight chain, play a major role in the increase of the hydraulic radius, and improve the temperature stability of the polymer solution.
3. Hydrophobic association [16]. Dodecyl ammonium bromide was introduced into the polymer, and the hydrophobic long chain formed a hydrophobic micro-region in the aqueous solution, which significantly increased the viscoelasticity of the polymer aqueous solution. For this kind of polymer, even if the molecular chain breaks during aging at high temperature, the existence of a steric hindrance effect of rigid groups makes the molecular chain movement resistance larger. The introduction of halogen and methyl increases the rigidity of the hydrophobic chain, making the hydrophobic carbon chain not easy to curl, which is conducive to the formation of intermolecular hydrophobic association structure. At the same time, this structure can shield the influence of some ions on the amide group, so as to improve the temperature resistance of the polymer.
4. Performance differences with other polymers. GTY-1 and GTY-2 polymers are quaternary polymers. The more monomers are added, the higher the total mass concentration of the material, the larger the molecular weight of the corresponding polymer, and the better the tackifying effect. The added raw materials include temperature-resistant monomers such as NVP, AMPS, DTAB and MAPTAC. The number of temperature-resistant groups contained in quaternary polymers GTY-1 and GTY-2 is higher than that of other polymers, and the strength of the spatial network structure formed is greater. MAPTAC and DTAB are introduced into the molecule, which makes the molecule contain rigid chain structure and strong temperature resistance.
5. NaAMPS is used in the synthesis of GTY-1 and GTY-2. Amps and NaAMPS are often used in the synthesis of high molecular polymers. The thickener was

synthesized with both as raw materials. The results are shown in Figure 6a,b. It can be seen from the figure that the rheological properties of the No. 1 and No. 2 polymers have little difference. At 120 °C, 100 s⁻¹, the viscosity is 54.69 mPa·s and 66.89 mPa·s, respectively; at 180 °C, 100 s⁻¹, the viscosity is 8.11 mPa·s and 8.65 mPa·s, respectively. From the figure, it can be seen that at 120 °C, 100 s⁻¹, the viscosity of the No. 1 and No. 2 polymers is 54.69 mPa·s and 66.89 mPa·s, respectively, and at 180 °C, 100 s⁻¹, the viscosity is 8.11 mPa·s and 8.65 mPa·s, respectively. It can be seen that the rheological properties of polymers 1 and 2 are similar, and amps and NaAMPS as reaction raw materials have little effect on the properties of polymers. However, from the rheological comparison results of No. 4 and No. 6, the viscosities of the No. 4 and No. 6 polymers at 120 °C and 100 s⁻¹ are 197 mPa·s and 258 mPa·s, respectively, and the viscosity of the No. 6 polymer is significantly higher than that of No. 4. The variables of the two are only amps and NaAMPS, but they are inconsistent with the results of No. 1 and No. 2, which is caused by the difference in molecular weight. The reason for the difference in molecular weight is the concentration. The reaction environment requires pH = 6, while amps is a strong acid, which needs to be adjusted by a certain amount of 40% NaOH solution, which will have a great impact on the material concentration in the solution.

6. It can be seen from Figure 6c,d that the viscosity loss rates of polymer No. 4 are 50.05%, 63.92%, 69.94% and 85.94%, respectively, and the viscosity loss rates of polymer No. 3 are 68.96%, 80.22%, 85.77% and 89.05%, respectively. This shows that the temperature resistance of polymer No. 4 is higher than that of polymer No. 3. The molecular chain of DTAB is longer than that of MAPTAC, the side chain of the synthesized polymer molecule is also larger, and the molecular volume of the synthesized polymer is larger. At the same time, because DTAB belongs to quaternary ammonium salts, its structure is a typical surfactant amphiphilic structure [11], containing hydrophilic groups. Therefore, the molecular hydration film of polymer No. 4 is thicker, stronger and more temperature-resistant. The performance difference between GTY-1 and GTY-2 is due to MAPTAC and DTAB, resulting in the stronger temperature resistance of GTY-2 than GTY-1.

3.3. Evaluation and Mechanism of Acid and Salt Resistance

In order to study the acid- and salt-resistance stability of the polymer, 10,000 mg/L of polymer solutions containing acid and salt (Ca²⁺, Mg²⁺) in different concentrations were prepared, and their viscosity was tested at 25 °C and 170 s⁻¹. The results are shown in Figure 7.

Figure 7a shows that the viscosity of polymer solution decreases with the increase of acid concentration, and then tends to be flat. The addition of hydrogen ion mainly affects the viscosity of polymer from two aspects: ① the effect of surface charge. The charge of hydrogen ion compresses the diffusion electric double layer on the surface of cationic polymer, or neutralizes with the anion carried by polymer, reduces the electrostatic repulsion between molecules, curls the molecular chain, enhances the hydrogen bonding within molecules, reduces the hydrodynamic radius and reduces the viscosity. This is particularly evident in cationic polyacrylamide such as in No. 1 and No. 2, whose viscosity loss rates are 94.36% and 92.94%, respectively. ② The oxidizability of H⁺ will attract the electrons in the common electron pair to a certain extent and affect the stability of the common electron pair, that is, H⁺ will “impact” the molecular chain, reduce the stability of polymer molecules and reduce the viscosity.

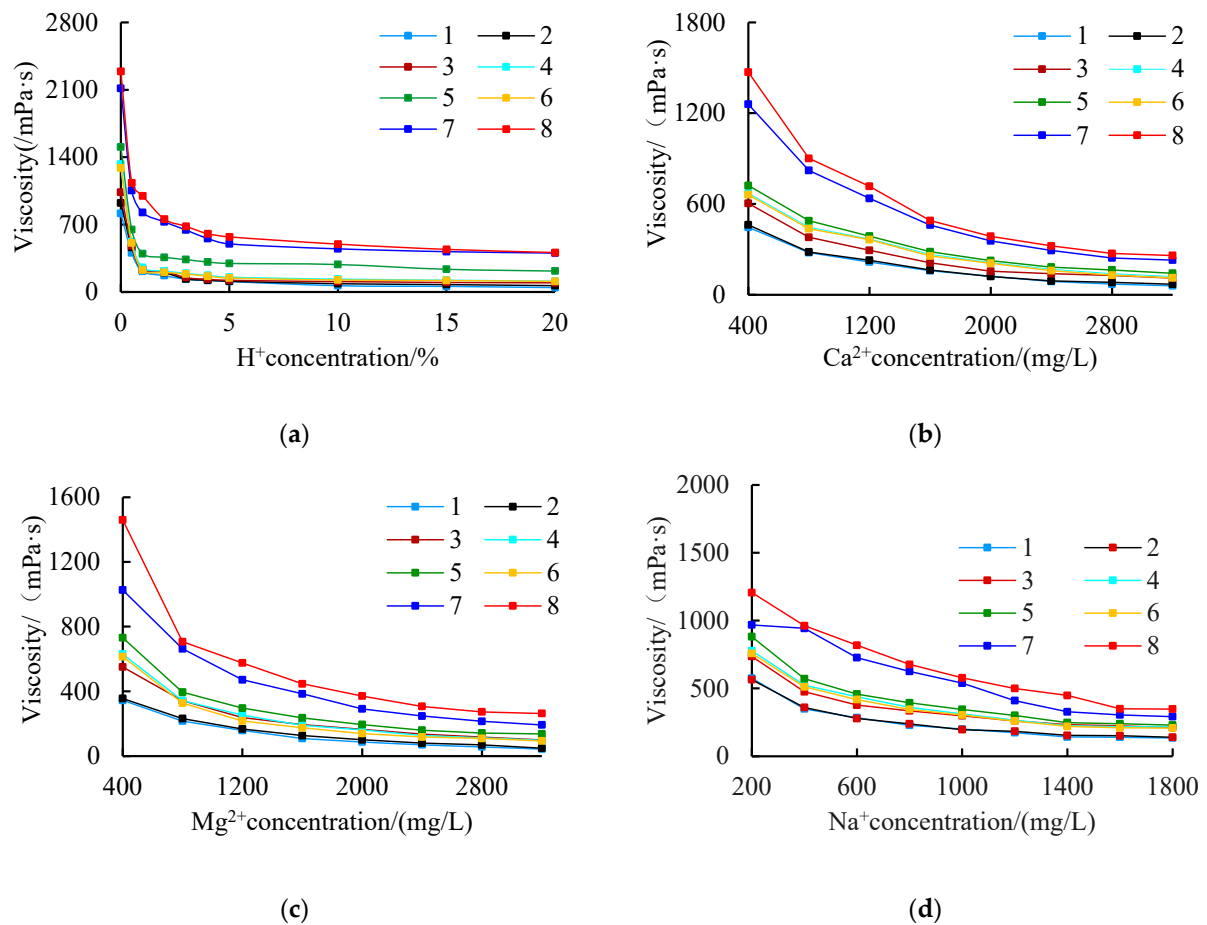


Figure 7. Acid- and salt-resistance stability of polymer. (a) Acid resistance stability; (b) VCa^{2+} stability; (c) Mg^{2+} stability; (d) Na^+ stability.

Under the condition of 20% acid concentration, the viscosity loss rate of the polymer is between 80 and 95%, the viscosity loss rates of GTY-1 and GTY-2 are the lowest, 80.88% and 82.14%, respectively, as is shown in Table 5, and the viscosity is 404.2 mPa·s and 409.4 mPa·s, respectively. In terms of viscosity loss rate and viscosity, GTY-1 and GTY-2 have good acid resistance and stability. This is affected such that the introduction of MAPTAC, DTAB and other rigid groups in the polymer molecules effectively enhances the steric hindrance of the polymer, strengthens the strength of the molecular chain, makes the molecular chain not easy to curl, or the degree of curl is small, the molecular chain is relatively stretched, the hydrodynamic radius is large, and the viscosity loss rate is small. Simultaneously, the introduction of long-chain molecules such as MAPTAC forms a certain hydrophobic association region, which shields the influence of the charge carried by some hydrogen ions on the molecular chain. In addition, due to the hydrophilicity of DTAB, the hydration film of the GTY-2 molecule is thicker than that of GTY-1, the solution effect of H^+ in the aqueous solution of GTY-2 is better, has a greater impact on the molecule, and weakens the hydrophobic effect to a certain extent. Thus, the acid resistance of GTY-2 is less and weaker than that of GTY-1.

Table 5. Viscosity loss percentage.

Type	1	2	3	4	5	6	GTY-1	GTY-2
20% HCl	94.36	92.94	90.86	91.58	85.59	91.56	84.90	85.89
3200 mg/L Ca ²⁺	86.67	84.88	81.82	82.02	80.46	83.12	81.78	82.36
3200 mg/L Mg ²⁺	87.26	86.28	81.80	84.45	81.16	84.76	81.20	81.91
3200 mg/L Na ⁺	75.69	73.29	69.68	72.03	72.89	72.45	68.53	71.03

As seen from Figure 7b–d, with the increase of inorganic salt ion concentration, the viscosity of the polymer solution gradually decreases and then tends to be flat. Electrostatic repulsion occurs between charged ions and macromolecular ions of magnesium ions; Concurrently, the dehydration of inorganic salt ions grabs the hydrated water around some copolymer chains, resulting in smaller hydrodynamic volume and lower viscosity. The viscosity loss rate of GTY-1 and GTY-2 is lower than that of other polymers because there are two S → O in the -SO₃H group, which belongs to the p-dm coordination bond. The ability of s to attract electrons from the -OH group is enhanced. The -OH group is easy to dissociate and belongs to strong acid. The -SO₃ ion group produced by dissociation is stable, has weak attraction to salt ions (positive ions), and has strong electrostatic repulsion (negative ions). The sulfonic acid group is not sensitive to salt, which can weaken the negative effect of metal ions on solution viscosity. At the same time, due to the introduction of macromolecules such as MAPTAC and DTAB, the steric hindrance is improved, and the shielding effect of hydrophobic groups on metal ions effectively reduces the influence of cations on the diffusion double layer and enhances the salt resistance of the polymer. Also, thanks to the salting-out effect of inorganic salt on hydrophobic groups, its hydrophobicity is enhanced and its solubility in aqueous solution is reduced. It is necessary to reduce the probability of contact with water through association with other hydrophobic groups, so as to increase the association between polymer molecules, increase the association strength and enhance the salt resistance. However, due to the introduction of DTAB, the polymer molecular side chain is hydrophilic, forming a thicker hydration film, increasing the contact probability between inorganic salt ions and water, and enhancing the effect of the compression diffusion electric double layer. Therefore, the salt resistance of GTY-2 is weaker than that of GTY-1.

3.4. Evaluation and Mechanism of Shear Resistance

In order to study the shear resistance of polymer molecules, in addition to the rheology of the polymer shown in Figure 6, prepare a 10,000 mg/L polymer solution, pour it into the warning blender constant speed mixer, shear it for 0, 20, 40, 60, 80, 100, 120, 140 and 160 min at 25 °C and 3500 r/min, and measure its viscosity after defoaming under a shear rate of 170 s⁻¹. The results are shown in Figure 8.

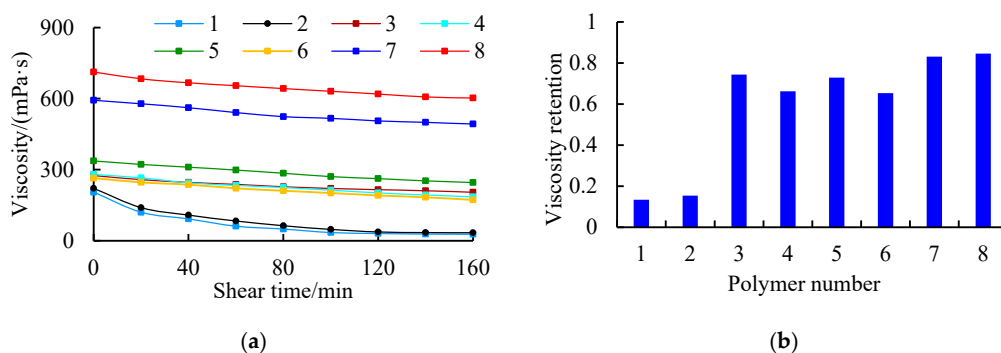


Figure 8. Experimental results of shear resistance of polymer. (a) Experimental results of shear resistance of polymer; (b) Viscosity retention after shearing for 180 min.

It can be seen from Figures 6 and 8 that the viscosity of the polymer decreases with the increase of shear speed and drunk shear time, and the reduction range is different. Figure 8 declares that the viscosity of the No. 1 and No. 2 polymers decreased most obviously, and the viscosity retention (the ratio of viscosity after shear to initial viscosity) was 13.35% and 15.35%, respectively, and the viscosity decreased significantly at the initial stage of mixing. This is because the influence of shear rate and shear time on a polymer aqueous solution is mainly reflected in the change of the physical crosslinking network of the polymer molecular chain caused by mechanical movements such as stirring and shear [15], which destroys the network structure between molecules and reduces the viscosity.

On the contrary, the viscosity retention of Nos. 3–8 is relatively high, with a minimum of 65% and a maximum of 83%. With the increase of shear time, the viscosity decreases slightly, especially GTY–1 and GTY–2. It shows that it has excellent shear resistance. This is due to the introduction of a large number of methyl groups in the molecular chain, which enhances the polarity and rigidity of polymer molecules, strengthens the effect on free water molecules, thickens the hydration film of polymer molecules, makes it easy to slide between hydration films, and enhances the resistance to shear force. At the same time, with the introduction of N and O atoms, a large number of hydrogen bonds have been formed in polymer molecules. Coupled with the electrostatic repulsion between polymer molecules, the state of polymer in aqueous solution is relatively curly. The structural damage of physical crosslinking in polymer solution caused by mechanical shear is small, and the viscosity drop is not obvious. To prove this, the polymer solutions of GTY–1 and GTY–2, No. 1, were sheared for 160 min and then scanned by scanning electron microscope. The results are shown in Figure 9. From Figure 9, we can clearly see the spatial network structure of GTY–1 and GTY–2. On the contrary, the structure of No. 1 was destroyed. After 160 min of shear, the spatial network structure in the solution is still strong, which proves the strong shear resistance of GTY–1 and GTY–2.

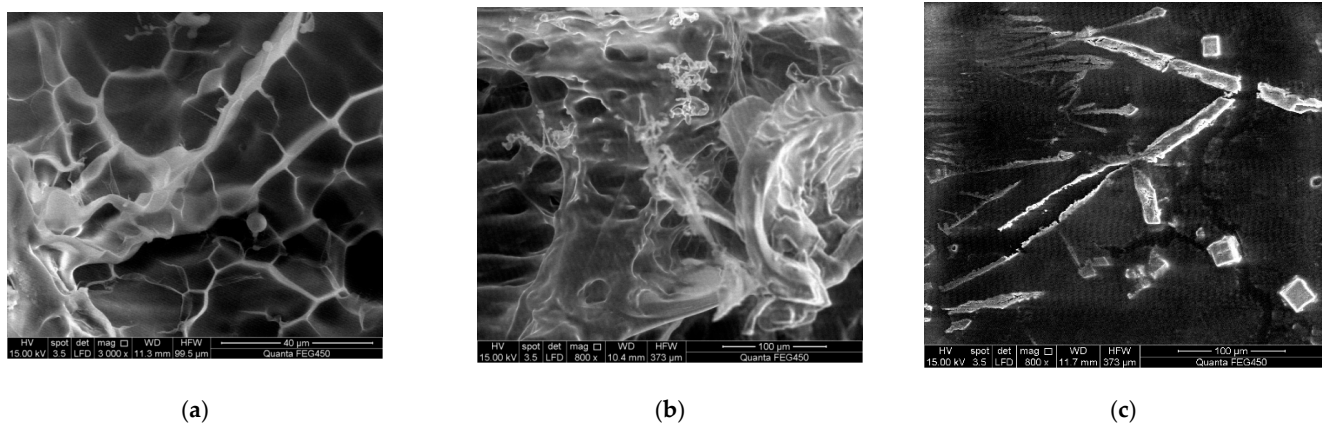


Figure 9. SEM of polymer solid powder. (a) GTY–1; (b) GTY–2; (c) No. 1.

It can also be seen from Figure 8b that the viscosity retention rates of GTY–1 and GTY–2 are 83.09% and 84.58%, respectively, indicating that the viscosity retention rate of GTY–2 is slightly higher than that of GTY–1. This is because the DTAB group introduced by the side chain of the GTY–2 molecule has good hydrophilicity, forms a thick hydration film and strengthens the sliding effect between polymer molecules. Therefore, GTY–2 has the strongest shear resistance.

4. Conclusions

The failure of thickeners at high temperature significantly reduces the acid fracturing effect. To solve the problem, eight types of binary, ternary and quaternary polymers were synthesized from AM, AMPS, NaAMPS, MAPTAC, DTAB and NVP. The polymers were characterized from the perspective of infrared spectrum and viscosity average molecular

weight. The temperature resistance, rheology and salt resistance and shear resistance of the synthesized polymers were compared. Based on our experimental results, the following conclusions are reached:

- (1) GTY–2 and GTY–1 have the highest molecular weight, 8.59×10^5 and 8.95×10^5 , respectively.
- (2) At 180 °C and 100 s^{-1} , the viscosity of GTY–2 is 181.52 mPa·s. The viscosity loss rate is 56.89%, and the temperature resistance is the best. GTY–1 has the second best temperature resistance, with a viscosity of 160.73 mPa·s and a viscosity loss rate of 60.70%.
- (3) GTY–1 and GTY–2 have the strongest acid and salt resistance. Due to the hydrophilicity of DTAB, the hydration membrane of the GTY–2 molecule is thicker than that of GTY–1, and the solution effect of H^+ and metal ions in the aqueous solution of GTY–2 is better, which has a greater impact on the molecule. Therefore, the acid and salt resistance of GTY–2 is slightly weaker than that of GTY–1.
- (4) The introduction of methyl groups in the molecular chain enhances the polarity and rigidity of polymer molecules. With the good hydrophilicity of DTAB groups, a thick hydrated film is formed, which enhances the resistance to shear force. Therefore, GTY–2 has the strongest shear resistance, followed by GTY–1.

In summary, GTY–1 and GTY–2 have better performance than the other 6 synthesized polymers. They can be used for thickening acid fracturing, which helps solve the current problem of thickener failure at high temperature in carbonate thickening acid fracturing.

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