

Synthesizing and Performance Test of a New Acidizing Gelatinizer ZCY-1

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Abstract

In order to meet the requirements of high temperature acidizing, a new acid gelatinizer was synthesized by choosing non ionic monomer AM, complex cationic monomer H-DMDAAC, anionic monomer AMPS as starting materials and redox system as initiator in aqueous solution at low temperature. Various factors influencing polymerization reaction were analyzed, the optimum conditions of polymerization were determined, the basic performance of gelling acid was evaluated and its action mechanism was studied. The results show that it has good property to increase viscosity, resistance to high temperature and acid-rock reaction retardation, the viscosity of acidizing fluid of 20% mass fraction can reach 37.5 mPa·s at the high temperature of 150°C and shearing rate of 170s-1 when the mass fraction of ZCY-1 is 1%; mass fraction of gelling acid remains 11.9% after 60 min's reaction with limestone, which is 7 times more than that of common acid, it can meet the need of acidizing in high temperature wells.

Key words: Acidizing; Gelatinizer; Polymerization; Viscosifying; High temperature resistance

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INTRODUCTION

With the continuous development of acidification technology, some of the complex acid, the potential acid, gel acid, fluoroboric acid, hot acid have been popularized

and applied^[1-3], so that the sandstone acidification process make great progress, but for deep well or high temperature wells acidification, small penetration depth, fast filtration speed, large hydraulic loss and other difficulties can not be effectively resolved, acidification often fails to achieve the intended purpose. In recent years, domestic and foreign extensively carried out research on thickeners, and mainly focused on the modification of acrylamide^[4-6]. In this paper, acrylamide as the main body, use redox reaction system, aqueous solution polymerization method, A kind of polymer thickener with a carbon-carbon as the main chain and linear type was synthesized. Among this thickener, the nonionic monomer AM is mainly to improve the molecular weight of the polymer, so that it has a good thickening property; the introduction of complex cationic pendant make the thermal stability of the polymer significantly increased; the introduction of sulfonic acid groups make the polymer have the ability that resisting attack of the external cationic and enhances the salt resistance of the polymer.

1. EXPERIMENTAL PART

1.1 The Main Experimental Equipment

Constant temperature water bath pot; DV-III+VISCOMETER viscometer; 50SL high temperature viscometer; electric mixer; electric blast drying oven; electronic balance; nitrogen cylinders and conventional glass equipment, etc..

1.2 The Main Experimental Drugs

Anionic monomer AMPS(2-acrylamido-2-methylpropanesulfonic acid), complex cationic monomer H-DMDAAC (made up of dimethyl diallyl ammonium chloride and methacryloyloxy ethyl trimethylammonium chloride), acrylamide, all are industrial products; oxidizing agent ammonium persulfate (analytically pure), reducing agent Sodium bisulfite (analytically pure), sodium hydroxide (analytically pure), ammonia (analytically pure),

urea (analytically pure), hydrochloric acid (industrial grade), Other additives (self-made) and the like.

1.3 Experimental Method

Adding anionic monomer AMPS and an appropriate amount of water to the beaker, adding equimolar sodium hydroxide to neutralize, then adding acrylamide and complex cationic monomer to adjust the pH of the system; then transferring the reaction mixture to the polymerizer, injecting nitrogen into the reaction mixture about 30min, adding the initiator system, sealed at a certain temperature after a certain period of time to get a glued viscous thick crude product; the crude product dissolved in water, with acetone precipitating it, then dissolving the precipitate in water, and then acetone Precipitating it again, so repeated 2-3 times, drying it until the mass is constant in a vacuum oven at 70°C, then crushing the solid powder to get powder-like ZCY-1 thickener.

2. RESULTS AND DISCUSSION

In this paper, the factors influencing the polymerization were investigated by single factor method. The ZCY-1 thickener was added to the hydrochloric acid solution with the mass fraction of 20% in the ratio of 1% (mass fraction), The influence of various factors on the

copolymerization was investigated based on the viscosity of the liquid at room temperature (30°C) and 170 s⁻¹ shear rate (there is no special description below, the evaluation conditions are above).

2.1 The Effect of Monomer Mass Fraction

For the free radical polymerization, due to the gel effect, the monomer mass fraction increases, the system viscosity increases, the long chain free radical curl, the active end may be wrapped, the termination rate is relatively reduced, the activity chain life is prolonged, the molecular weight increases, acid viscosity increase. However, the increase of monomer mass fraction may produce the opposite result. The polymerization heat can not be dispersed in time, the temperature of the system is increased and the speed of initiation is accelerated, and the molecular weight of the copolymer decreases. Therefore, the viscosity of copolymer acid increased with the monomer mass fraction, and the maximum value appeared, The effect of monomer mass fraction on acid viscosity is shown in Figure1. It can be seen from Figure 1, with the increase in monomer mass fraction, acid viscosity increased first and then decreased, about 20% to reach the maximum, acid viscosity reached 66.5 mPa·s, then decreased, therefore, Monomer mass fraction of about 20% is appropriate.

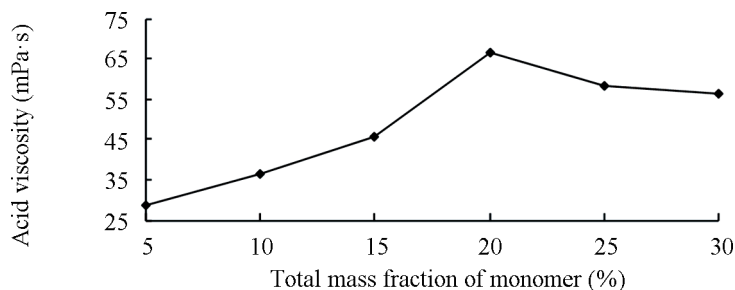


Figure 1
Effect of Monomer's Mass Fraction on Acidizing Fluid's Viscosity

2.2 The Effect of the Initiator

Acidification thickener is an important indicator of the solubility, and many monomers in the low temperature conditions can be a good way to avoid cross-linking, branching and other side effects, get better quality polymers, Effects of different initiators on polymerization is shown in Table 1. From Table

1, the higher conversion rate can be obtained by the polymerization initiated by oxidation-reduction system, and higher acid viscosity can be obtained. When the amount of initiator reaches 0.3% (mass fraction), the conversion rate is 92.3%, Acid viscosity is 68.5 mPa·s. Therefore, this paper chooses the oxidation-reduction system as the initiating system.

Table 1
Effect of Initiator on Transformation Ratio and Acidizing Fluid's Viscosity

Type of Initiation system	The dosage of initiator (%)	Conversion rate (%)	Acid viscosity (mPa·s)
AIBN	0.1	75.2	42.5
	0.2	79.4	47.2
	0.3	83.2	51.6
Ammonium persulfate	0.1	79.4	46.5
	0.2	81.2	49.8
	0.3	85.1	52.6
Ammonium persulfate and sodium bisulfite (molar ratio 1:2)	0.1	88.2	57.6
	0.2	91.2	62.4
	0.3	92.3	68.5

2.3 The Effect of Monomer Ratio

2.3.1 The Effect of Anionic Monomers

In the polymerization reaction, the monomer ratio is an important factor affecting the performance of the polymer. When the influence of the anionic monomer is investigated, the mole percentage of the immobilized cationic monomer is 10% and the mole percentage of the anionic monomer is increased (decrease the mole

percentage of AM correspondingly), to study the viscosity changes of product in the acid solution, the results shown in Table 2. From Table 2, acid viscosity increased with the increase in the amount of AMPS, synthesising it when the mole fraction is 35%, acid viscosity reached a maximum of 64.7 mPa·s, continue to increase its proportion, the viscosity of the acid solution tends to remain unchanged, its dosage control is 35%.

Table 2
Effect of Monomer Ratio on Acidizing Fluid's Viscosity

Serial number	Anionic monomer (%)	Acrylamide (%)	Composite cationic monomer (%)	Acid viscosity (mPa·s)
1	10	80	10	32.8
2	15	75	10	38.4
3	20	70	10	42.2
4	25	65	10	51.5
5	30	60	10	58.3
6	35	55	10	64.7
7	40	50	10	64.2
8	35	60	5	67.1
9	35	55	10	64.7
10	35	50	15	58.8
11	35	45	20	53.4
12	35	40	25	47.1

2.3.2 The Effect of Complex Cationic Monomers

When the influence of the complex cationic monomer was investigated, the mole percentage of the immobilized anionic monomer was 35%, and changing the mole percentage of the complex cationic monomer (the mole percentage of the AM was changed correspondingly), to study the viscosity change of the product in the acid solution. The results are shown in Table 2. From Table 2, with the increase in the amount of H-DMDAAC, acid viscosity gradually reduced, but the introduction of H-DMDAAC main purpose is to make the molecular chain have a larger pendant, and enhance the rigidity of the molecular chain, making The thermal stability of polymer molecules increased, taking into account its resistance to temperature performance and cost, Control

its dosage in 10%.

2.4 The Effect of pH Value in System

In the copolymerization reaction, the pH value will affect the reactivity rate of each monomer, so it will affect the reaction rate and the structure and properties of the polymer. In this paper, the pH value is adjusted with ammonia, and when the aqueous solution contains AM and NH₃, nitrogen three propenamide will generate, nitrogen three propenamide as a reducing agent at a lower temperature with an oxidizing agent to form an oxidation-reduction system to initiate AM polymerization, and nitrogen three propenamide simultaneously serves as a chain transfer agent to improve the solubility of the polymer. The effect of pH on the viscosity of the polymer acid is shown in Figure 2.

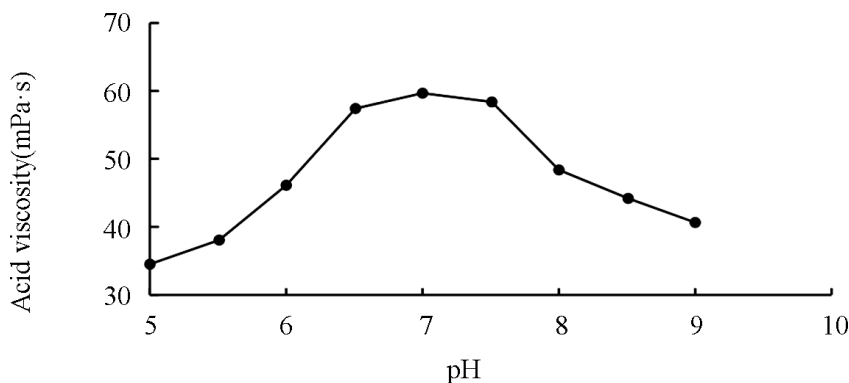


Figure 2
Effect of pH on Acidizing Fluid's Viscosity

It can be seen from Figure 2, in the neutral conditions of synthesis, acid viscosity reached a maximum of 59.8

mPa·s, so the selected pH value of 7.0 for synthesis. This is because the polymerization at higher pH values need

to add a larger amount of ammonia, chain transfer rate is too large, it's difficult to form large molecules; and polymerization at the lower pH value, will be associated with intramolecular and Intermolecular imide reaction, forming branched or cross-linked polymer, and in neutral conditions can obtain the products with high relative molecular weight, acid viscosity will reach the maximum value.

2.5 The Effect of Reaction Temperature

The reaction temperature is much lower than that of the single oxidation system, and the low temperature condition is also meaningful to improve the molecular weight of the polymer. However, the reaction temperature is too low for the reaction kinetics is unfavorable, so the temperature is also an important factor in the synthesis of polymers, the reaction temperature on the viscosity of the acid as shown in Figure 3.

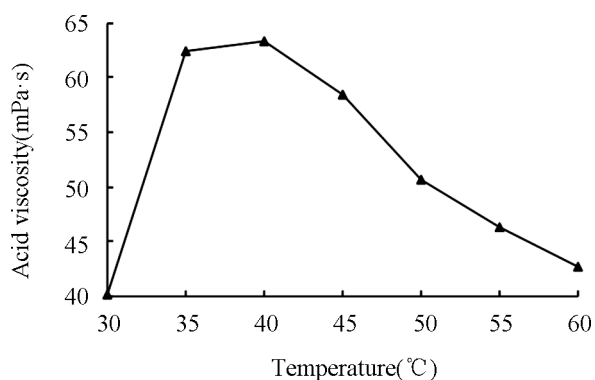


Figure 3
Effect of Reaction Temperature on Acidizing Fluid's Viscosity

Available from Figure 3, with the increase of the reaction temperature, the viscosity of the polymer in the acid increased first and then decreased. When the temperature was 40 s, the viscosity of the acid reached the maximum value of 63.4 mPa·s. The reason for this phenomenon is that with the increase of the reaction temperature, the decomposition rate of initiator increased, resulting in the reaction system of free radicals increased, polymerization rate, monomer conversion rate is high, but at a certain temperature, the monomer conversion rate

Table 3
Effect of Mass Fraction of Thiocarbamide on Acidizing Fluid's Viscosity

Thiocarbamide mass fraction (%)	0	0.5	1.0	1.5	2.0
Polymer dissolution time (min)	34	25	20	17	13
Viscosity (mPa·s)	64.3	60.2	58.1	57.2	56.3

It can be seen from Table 3 that the dissolution rate of the polymer is greatly improved by the addition of thiocarbamide, and the molecular weight of the polymer decreases with the addition of thiocarbamide. According to the theory of instant, if the polymer contains small

changed little with the increasing of reaction that produced free radicals increased, will lead to the decrease in degree of polymerization, the molecular weight of products decreased, but when the temperature is too low, so that the temperature of initiator decomposition becomes difficult, can not fully response. In this paper, the optimal reaction temperature is 35- 40°C.

2.6 The Effect of Reaction Time

Different polymerization time, the viscosity of the acid is not the same, as shown in Figure 4. As can be seen from Figure 4, when the reaction time was 10 h, the viscosity of the acid solution reached 64.7 mPa·s, and the reaction time was prolonged. The viscosity of the acid increased slowly, and it was almost unchanged. This is because with increasing reaction time, monomer concentration and initiator concentration decreased, the viscosity increased, monomer free radicals and reduce the chance of contact, thus affecting the monomer conversion rate, when the reaction is carried out to a certain time, continue to extend the time, the conversion rate tends to be constant. Considering the production cycle, the final reaction time is 10-12 h.

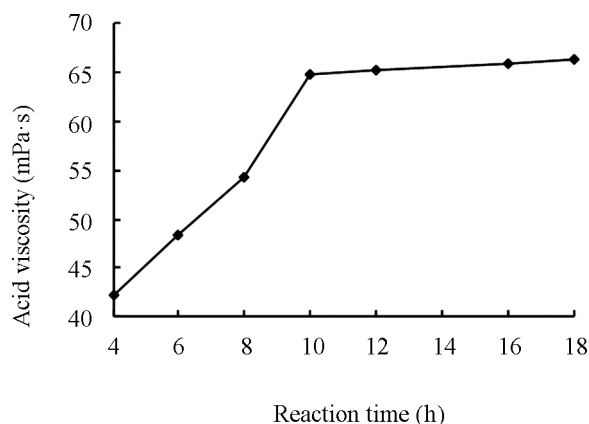


Figure 4
Effect of Reaction Time on Acidizing Fluid's Viscosity

2.7 The Effect of Thiocarbamide Addition

Thiocarbamide, as a kind of synthetic additives, is commonly used in the polymerization process of AM, and the effect of thiocarbamide content (mass fraction) on the performance of polymer acid solution is shown in Table 3.

molecular structure similar, the dissolution rate of the small molecule can accelerate the polymer in the solvent, thus adding dissolution properties of thiocarbamide is benefit to AM polymerization products of discrete molecular polyacrylamide water-soluble polymers

between direct hydrogen bonding, improve closely conformation, promote the water and the solution viscosity, while urea can be used as auxiliary reducing agent, participate in the redox reaction process. But the chain transfer reaction of thiocarbamide, the effect of kinetic chain length, so that the molecular weight of the polymer decreases, the viscosity is reduced in acid solution, comprehensive consideration of various factors, and ultimately determine the amount of thiocarbamide is about 0.5%.

3. THE MAIN PERFORMANCE TEST OF GELLING ACID

3.1 Adhesion Property

According to SY/T6214-1996 “viscosifying agent evaluation method”, formulated a series of different concentrations of gelling acid samples, the mass fraction of ZCY-1 thickener is 0.2%, 0.4%, 0.6%, 0.8%, 1% and 1.2% respectively, hydrochloric acid concentration was 20%. Measured at room temperature (30 degrees C), 170s-1 shear rate viscosity, the results shown in Figure 5.

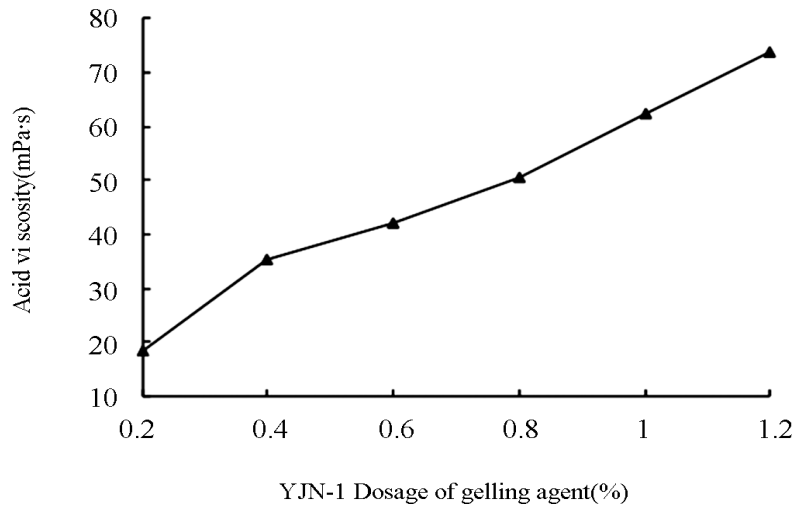


Figure 5
Relationship Between Gelatinizer’s Mass Fraction With Acidizing Fluid’s Viscosity

As can be seen from Figure 5, with the increase of the mass fraction of the thickener, the viscosity of the acid solution is increased. When the mass fraction of the thickener is 1.2%, the viscosity of the acid solution is 73.6 mPa to s at room temperature, and the viscosity of the solution increases obviously.

The thermal stability of SY/T5754-1995 acid solution was evaluated according to the standard of thermal stability. The optimal conditions of synthesis of the thickening agent is added to the mass fraction of 20% hydrochloric acid, measured at 170s-1 shear rate, gel under different temperature conditions the acid viscosity, and compared with gelled acid (commonly used for quality score sheet), as shown in Table 4.

3.2 Temperature Resistance

Table 4
Character of Temperature Resistance of Gelling Acid

	Temperature (°C)					Remarks
	30	60	90	120	150	
Acid viscosity (mPa·s)	58.8	49.3	40.2	28.5	19.6	1.5% VY-101 Gelled acid
	56.2	40	32.4	19.8	15.2	4% CTI-9 Gelled acid
	62.4	54.5	48.6	42.2	37.5	1% ZCY-1 Gelled acid

From Table 4 can be increased with temperature, the acid viscosity gradually decreased, but at high temperature under 150 DEG C, ZCY-1 gel 1% acid viscosity is still 37.5 mPa·s, and VY-101 1.5% gelled acid is only 19.6 mPa·s, CTI-9 4% gel acid only 15.2 mPa·s, ZCY-1. Thickener high temperature resistance is better, and with less, suitable for high temperature deep well acidizing.

3.3 Retarding Performance

In this paper, the reaction rate of thickener is reflected by the concentration of residual acid after the reaction of gelled acid and limestone. Specific experimental steps: Preparation of mass fraction 20% (ZCY-1 acid gel thickener concentration was 1%, CTI-9 thickening agent mass fraction of 4%), under the condition of 90 DEG

C content than the static 1:4 condition and limestone reaction, every time out a small amount of acid titration with standard NaOH solution, so as to obtain the residual

concentration acid. The results were compared with that of the blank hydrochloric acid and limestone. The results are shown in Table 5.

Table 5
Retarding Performance of Gelling Acid

	Time(min)							Remarks
	0	10	20	30	40	50	60	
	20	13.5	8.3	6.1	2	1.36	0.8	Blank hydrochloric acid
Acid mass fraction (%)	20	16	11.7	9.5	5.3	3.8	2.6	4% CTI-9 gelled acid
	20	18.7	15.2	13.3	11.9	8	5.8	1% ZCY-1 gelled acid

From Table 5 can be obtained, when 40 min is close to the blank of spent acid, CTI-9 acid gelling concentration was 5.3%, ZCY-1 gelled acid is 11.9%, acid after 60 min and high concentration of acid, 60 min acid concentration is 7 times more than the ordinary acid, ZCY-1 gelled acid corrosion speed performance is very good, is conducive to the formation of deep penetrating acid.

(c) Delayed mechanism: the main reason of ZCY-1 gelled acid can achieve slow is the ambassador ZCY-1 molecular weight acid viscosity increases, the liquid limit of convection, the ion transfer to diffusion, thus delaying the reaction rate and acid rock, increasing acidification radius, which caused cracks extending to the deep distance. The communication channel to produce better, achieve the purpose of deep acidification.

4. ACTION MECHANISM

According to polymer theory, the mechanism of ZCY-1 is as follows:

(a) Thickening mechanism: The synthesis of carbon-carbon backbone, linear polymer, containing many charged and hydrophobic groups on the macromolecular chain, hydration of intramolecular electric repulsion and the polar groups of the molecular chain is loose and extended state, when the polymer reaches a certain critical concentration hydrophobic interaction, intermolecular hydrogen bond, and Coulomb interaction in the molecular chain cross-linked to form a space truss structure has a certain strength, have very strong tackifying effect.

(b) The mechanism of temperature resistance: In this paper, the synthesis of high molecular weight chain containing pyrrolidine ring, increase the rigidity of the polymer chain, improve the heat resistance of polymer. The side chain contains a strong polar group -NH₂, so that hydrogen bonds between molecules, are conducive to the crystallization of polymer, polymer molecular chain interaction between large, high energy required to destroy the polymer is also great.

REFERENCES

- [1] Gao, J. C., Peng, Z., & Lin, H., et al. (2002). Synthesizing and performance test of XPI2-1 viscous acid's thickener. *Journal of Xinjiang Petroleum Institute*, 12(4), 26-28.
- [2] Zou, Y. B., Zhou, L. B., & Pei, C., et al. (2003). Optimized research and application of slow reacting acid of high temperature and deep layer. *Oil Drilling & Production Technology*, 25(4), 61-63.
- [3] Ali, S. A. (2006). *Effective stimulation of high-temperature sandstone formations in east venezuela with a new sandstone-acidizing system*. SPE 98318.
- [4] Chike, U. (2004). *Solvent/acid blend provides economic single step matrix acidizing success for fines and organic damage removal in sandstone reservoirs: A niger-delta case study*. SPE 90798.
- [5] Pongratz, R. (2005). *Optimizing matrix acid treatments in a multi-layered reservoir in Russia by applying different diversion techniques*. SPE 94485.
- [6] Olav, M. (2004). *Gelled organic acid system for improved CaCO₃ removal in horizontal openhole wells at the heidrun field*. SPE 90359.