

Article

Development and Characterization of Environmentally Responsive Thickening Agents for Fracturing Fluids in Shale Gas Reservoir Stimulation

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Abstract: In response to the special requirements for shale gas reservoir stimulation, a novel environmentally responsive fracturing fluid thickener was designed and developed in this paper. N,N-dimethylhexadecylallylammonium chloride (C16DMAAC), N-vinylpyrrolidone (NVP), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), and Acrylamide (AM) were used as functional monomers, and the synthesis of the target product was achieved successfully through free radical polymerization in an aqueous solution. The findings indicated that in the optimized situation, where the total monomer mass fraction was 25%, the ratio of AM:AMPS:C16DMAAC:NVP was 15:10:3:2, the initiator mass fraction was 0.3%, the pH was 6.5, and the temperature was 60 °C, the thickener achieved a number-average molecular weight of 1.13×10^6 . Furthermore, its remarkable thermal stability was manifested, as it only experienced a 15% mass loss in the temperature interval spanning from 40 °C to 260 °C. Performance evaluation results indicated that, at 120 °C, the viscosity of the thickener under study increased by over 49% compared to the control group. Simultaneously, in a 0.4 wt% CaCl₂ environment, it retained a high viscosity of 54.75 mPa·s. This value was 46.61 mPa·s greater than that of the control group. Furthermore, under the conditions of a temperature of 170 °C, the fracturing fluid viscosity remained above 68 mPa·s. Regarding the flow performance, within the flow rate range from 110 to 150 L/min, it showed a remarkable drag reduction effect, achieving a maximum drag reduction rate of 70%. At 150 °C, the fracturing fluid exhibited superior proppant-carrying efficacy, with a settlement rate that was 26.1% lower than that of the control group. The viscosity and residue content of the gel-broken fracturing fluid exceeded the requirements of industry standards. In particular, the residue content of this fracturing fluid was 21% lower than that of the control group. The research results provide an environmentally responsive fracturing fluid thickener with excellent performance for shale gas reservoir stimulation.

Keywords: shale gas; fracturing fluid thickener; environmental response; performance evaluation



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1. Introduction

In the current era, as the global energy structure is being adjusted and the development of clean energy is advancing at an accelerated pace, shale gas, which is a crucial

unconventional natural gas resource, has increasingly emerged as a focal point of research and development within the energy domain [1–3]. Shale gas resources are abundant in China. Nevertheless, on account of the reservoir features such as low permeability, low porosity, and high heterogeneity, large-scale hydraulic fracturing technology is frequently necessary to realize economically feasible exploitation [4–6]. In this process, fracturing fluid, as a key medium for construction, its rheological properties and proppant-carrying capacity directly determine the fracturing effect and shale gas recovery rate.

Thickeners commonly used in traditional fracturing fluids, such as natural plant gums represented by guar gum and their derivatives, can play a certain role in viscosity enhancement in conventional reservoir fracturing [7–9]. However, when faced with the complex and variable geological conditions of shale gas reservoirs and the increasingly stringent environmental requirements, obvious deficiencies have emerged. For instance, in high-temperature environments, the hydroxyl groups within the molecular chain of guar gum are highly susceptible to oxidative degradation. This leads to a significant decline in the fracturing fluid viscosity and a subsequent reduction in its proppant-carrying capacity. At the same time, with the increase in the amount of thickener used, the residues generated after gel breaking are not easy to completely flow back in the reservoir, which is likely to block pores and fractures, ultimately reducing reservoir permeability and causing irreversible damage [10].

In recent years, synthetic polymer thickeners have increasingly drawn the attention of researchers. This is because they possess advantages like a strong viscosity enhancement capacity, excellent gel-breaking performance, and low residue, which can help deal with the challenges that extreme environments, such as high temperature and high salinity, pose to the performance of fracturing fluids [11,12]. By means of molecular design, specific functional groups are incorporated into the molecular chain of the polymer. This makes it possible for the polymer to react to environmental factors like ionic strength, temperature, and pH value, thus realizing the intelligent control of the rheological characteristics of the fracturing fluid. Among them, polymers with AMPS and AM as the main monomers have outstanding performance in temperature resistance and salt resistance [13–15], providing new ideas for optimizing the formula of shale gas fracturing fluids.

To further improve the comprehensive performance of polymer thickeners, this paper introduces two comonomers, N,N-dimethylhexadecylallylammonium chloride (C16DMAAC) and N-vinylpyrrolidone (NVP). C16DMAAC, a monomer featuring a long-chain alkyl structure, possesses hydrophobic properties. Within the polymer molecular chain, these properties promote the creation of a microphase separation structure. As a result, not only is the stability of the polymer enhanced, but also its capacity to adjust the rheological characteristics of the fracturing fluid is improved [16,17]. At the same time, appropriate hydrophobicity can also improve the distribution and compatibility of the polymer in the reservoir and reduce the risk of residue blockage. NVP, due to its unique pyrrolidone ring structure, significantly improves the water solubility and low-temperature fluidity of the polymer, and is also conducive to improving anti-degradation ability and the temperature resistance of the polymer [18,19], which is crucial for maintaining the efficient operation of the fracturing fluid under extreme reservoir conditions.

In light of the aforementioned background, this paper aims to use four comonomers, AM, AMPS, C16DMAAC, and NVP, as raw materials to synthesize an environmentally responsive thickener (ERT) for shale gas reservoir stimulation through an aqueous solution free radical polymerization method, and systematically study its molecular structure, rheological properties, temperature and salt resistance, and gel-breaking effect. The research aims to develop a thickening agent that can fully adapt to the harsh operating conditions

of shale gas reservoirs and simultaneously possess the characteristics of high viscosity enhancement, low residue, and intelligent response.

2. Design of Experiments

2.1. Experimental Materials

The main materials used in this experiment are as follows: analytical grade reagents, including AM, AMPS, C16DMAAC, NVP, potassium persulfate ($K_2S_2O_8$), sodium bisulfite ($NaHSO_3$), sodium hydroxide ($NaOH$), and absolute ethanol, all of which were purchased from Chengdu Anshide Company (Chengdu, China). High-purity nitrogen was used for deoxygenation. Self-made reagents include an organic zirconium crosslinker, which was prepared by controlled hydrolysis and condensation of zirconium tetrabutoxide [$Zr(Obu)_4$] and γ -aminopropyltriethoxysilane in absolute ethanol, an organic acid crosslinking accelerator formulated with citric acid in absolute ethanol, and a breaker with ammonium persulfate as the main component. In addition, the ceramsite (particle size 0.38–0.83 mm, 20–40 mesh) was provided by Henan Xiangsheng Ceramsite Company (Zhengzhou, China).

2.2. Experimental Apparatus

In this study, the following main instruments were employed for the structural and property testing of samples: A Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer was used for FTIR analysis. A Bruker AVANCEIIIHD nuclear magnetic resonance (NMR) spectrometer was utilized for 1H -NMR analysis to determine the molecular structure. The molecular weight was measured through GPC analysis, for which the Shimadzu GPC-20A system was utilized. A Linseis TGA PT1000 thermogravimetric analyzer was utilized to test thermal stability. A Brookfield DV2T viscometer was used to measure its viscosity. The drag reduction effect of the fracturing fluid was tested using an SLSY 1849 fracturing pipeline drag reduction instrument. In addition, the drying treatment of all samples was carried out in a TST101A 1B electrothermal constant-temperature forced-air drying oven produced by Chengdu Test Instrument Co., Ltd. (Chengdu, China), and the mixing operation was completed using a JJ 1 precision power-increasing electric stirrer from Changzhou Surui Instrument Co., Ltd. (Changzhou, China). The associated equipment is shown in Figure 1.



Figure 1. Experimental apparatus physical diagram.

2.3. Preparation of Thickening Agent and Formulation of Fracturing Fluid

2.3.1. Preparation of Thickening Agents

(1) Solution Preparation: Add 100 g of distilled water into a glass bottle with screw threads. Accurately weigh the monomers of AM, AMPS, CD16, and NVP according to the predetermined ratio, and add them into the bottle in sequence. Start the constant-speed stirring device and keep stirring until all monomers are completely dissolved, forming a homogeneous mixed monomer solution.

(2) pH Adjustment and De-oxygenation Treatment: After the monomers are completely dissolved, precisely adjust the pH of the solution to neutrality using 2 mol/L NaOH solution. Place the glass bottle in cold water to lower the solution temperature to room temperature. Simultaneously, high-purity nitrogen is introduced into the solution for 30 min to thoroughly eliminate the dissolved oxygen within the solution, thereby precluding its interference with the subsequent polymerization reaction.

(3) Initiation of Polymerization Reaction: After the de-oxygenation treatment is completed, add a predetermined amount of $K_2S_2O_8$ and $NaHSO_3$ into the solution as initiators, and keep stirring until they are completely dissolved. Seal the glass bottle and then submerge it in a 45 °C constant-temperature water-bath for an 8 h reaction. This allows the monomers to polymerize into a viscoelastic polymer gel block within an oxygen-free setting.

(4) Polymer Post-treatment: After the reaction is completed, place the obtained polymer gel block in anhydrous ethanol. Cut it into small pieces with scissors for subsequent washing. Wash the broken gel particles repeatedly with anhydrous ethanol to remove unreacted monomers and impurities. Transfer the washed white solid particles to a TST101A 1B electro-thermal constant-temperature forced-draft drying oven and dry them at 60 °C until a constant weight is achieved. Grind the dried solid into powder to obtain a fracturing fluid thickener sample for subsequent performance testing and characterization.

The polymerization reaction equation is shown in Figure 2.

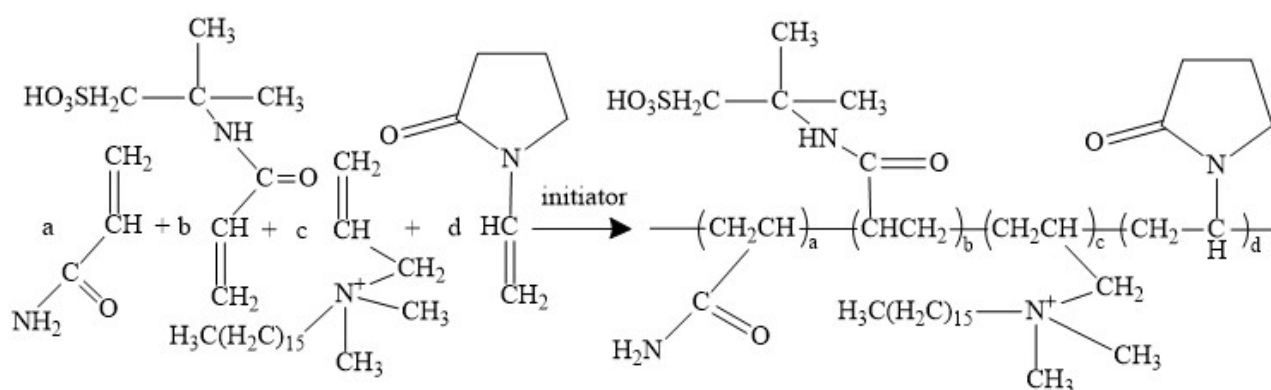


Figure 2. The grafting technical approach of ERT.

2.3.2. Preparation of Fracturing Fluid

(1) Preparation of base fluid: The thickener (AM/AMPS/C16DMAAC/NVP copolymer, 0.45%) was slowly and uniformly added into tap water under a stirring speed of 3000 r/min. The mixture was stirred for 10 min until the thickener was completely dissolved, resulting in a transparent and homogeneous thickened liquid.

(2) Static aging: The thickened liquid that had been prepared was put into a 30 °C water bath and allowed to stand for a duration of 4 h. During this time, the thickener fully absorbed water and swelled, forming a stable thickening system.

(3) Preparation of cross-linked system: Under continuous stirring, 0.025% of the organic zirconium cross-linker BPA was slowly added to the thickened liquid. The mixture underwent stirring for 5 min so as to ensure its uniform dispersion.

(4) pH adjustment: To create a favorable environment for the cross-linking reaction, a pH regulator in the form of 0.015% citric acid was added. This addition adjusted the pH of the solution to the range between 4.0 and 4.5.

(5) Uniform mixing: Stirring was continued for 10 min until a stable cross-linked gel was formed. Thus, the preparation of the fracturing fluid was completed, and it could be used for subsequent performance tests.

2.3.3. Optimization of Synthesis Conditions

Based on the principle of free radical polymerization, numerous factors exert a substantial impact on the properties of copolymers, with the main ones being as follows:

(1) Monomer molar ratio (r): The molar ratio of AM, AMPS, C16DMAAC, and NVP determines the structure and properties of the copolymer.

(2) Monomer mass fraction (w_1): It affects the final concentration and molecular weight distribution of the polymer.

(3) Initiator mass fraction (w_2): It directly impacts the free radical concentration, thereby influencing the polymerization rate and the molecular weight of the copolymer.

(4) pH value of the reaction system: It affects the ionization state of monomers and the activity of the initiator, thus influencing the polymerization behavior.

(5) Reaction temperature (T): It determines the activation energy of the polymerization reaction and the generation rate of free radicals and has a crucial impact on the conversion rate and structure of the copolymer.

To systematically investigate the comprehensive effects of these factors on the properties of copolymers, an orthogonal experimental design with 5 factors and 4 levels was adopted in this study. Through rational determination of levels and combinations, statistically significant results were derived. These results were utilized to identify the crucial factors affecting the properties of copolymers and their optimal conditions. Consequently, they established the foundation for the performance improvement of copolymers. The factors and levels are shown in Table 1.

Table 1. Factor-Level Table for Orthogonal Experiment.

Levels	Factors				
	r	pH	w_2 (%)	w_1 (%)	T (°C)
L1	10:8:2:2	4.5	0.1	10	45
L2	12:6:1:1	5.5	0.2	15	50
L3	15:10:3:2	6.5	0.3	20	55
L4	18:12:4:2	7.5	0.4	25	60

The fracturing fluid viscosity at 120 °C and a shear rate of 170 s^{−1} was used as the evaluation index. Under the experimental conditions of that group, a better thickening performance of the thickener is indicated by a higher apparent viscosity (Table 2).

Table 2 shows that the factors influencing the high-temperature viscosity of the thickener, ranked from the most to the least important, are as follows: monomer mass fraction (w_1) > initiator mass fraction (w_2) > monomer molar ratio (r) > pH value > reaction temperature (T). The following represent the optimal synthesis conditions: pH = 6.5, monomer molar ratio r = 15:10:3:2, monomer mass fraction w_1 = 25%, initiator mass fraction w_2 = 0.3%, and reaction temperature T = 60 °C.

Table 2. Table for Orthogonal Experiment.

No	r	w ₁ (%)	w ₂ (%)	pH	T (°C)	Viscosity (mPa·s)
T1	L1	L1	L1	L1	L1	20.47
T2	L1	L2	L2	L2	L2	34.58
T3	L1	L3	L3	L3	L3	56.86
T4	L1	L4	L4	L4	L4	64.40
T5	L2	L1	L2	L3	L4	41.45
T6	L2	L2	L1	L4	L3	31.90
T7	L2	L3	L4	L1	L2	30.47
T8	L2	L4	L3	L2	L1	42.25
T9	L3	L1	L3	L4	L2	47.37
T10	L3	L2	L4	L3	L1	46.55
T11	L3	L3	L1	L2	L4	54.19
T12	L3	L4	L2	L1	L3	55.33
T13	L4	L1	L2	L2	L3	35.92
T14	L4	L2	L1	L1	L4	35.62
T15	L4	L3	L4	L4	L1	41.36
T16	L4	L4	L3	L3	L2	53.44
K ₁	44.07	36.30	35.54	35.47	37.66	
K ₂	36.52	37.16	41.82	41.74	41.47	
K ₃	50.86	45.72	49.98	49.57	45.00	
K ₄	41.58	53.85	45.69	46.26	48.91	
R	14.34	17.55	14.44	14.10	11.25	

Where K_i denotes the mean of the experimental results at the level of the current factor *i* and R denotes the extreme deviation of the current factor.

2.4. Characterization Methods for the Structure of Thickening Agents

The molecular structure of the thickener was characterized using a Nicolet-6700 infrared spectrometer. The dried thickener powder was mixed with KBr, ground, and pressed into thin flakes, followed by scanning on the infrared spectrometer. The scanning range was 400–4000 cm^{−1}, with a resolution of 4 cm^{−1}. By analyzing the positions and intensities of characteristic absorption peaks in the infrared spectrum, the functional groups contained in the thickener molecules were determined, and whether the molecular structure conformed to expectations was verified.

The Shimadzu GPC-20A system was employed to measure the polymer molecular weight by GPC. The mobile phase employed was an aqueous solution of 0.1 mol/L NaNO₃, flowing with a rate of 0.5 mL/min. Prior to injection for analysis, the sample was filtered using a 0.45-micrometer-pore-size membrane. Detection was carried out using a differential refractive index detector. The research was carried out at 30 °C, with an injection volume set at 100 µL. To guarantee data reliability, each sample underwent measurement three times. Eventually, crucial parameters including the Mn, Mw, and polydispersity index were acquired.

¹H-NMR spectrum analysis of the thickener was performed using a Bruker AVANCE III HD NMR spectrometer. Deuterium oxide (D₂O) was used as the solvent. A small amount of the sample was dissolved and transferred into a NMR test tube, and the ¹H-NMR spectrum of the thickener was recorded at 25 °C.

2.5. Evaluation of the Performance of Thickening Agents

A Linseis TGA PT1000 thermogravimetric analyzer was employed in this test. A 10 mg sample of the thickener was placed in the crucible of the thermogravimetric analyzer. The temperature was incrementally elevated from 25 °C to 600 °C, and the rate was 10 °C/min. The change in the sample mass with respect to temperature was recorded all the way. Then, by analyzing the thermogravimetric curve, the mass loss rates of the thickener at

different temperature points were figured out, for the purpose of evaluating its thermal stability property.

The viscosity changes in thickeners at different concentrations and temperatures were measured using a Brookfield DV2T viscometer. The shear rate was 170 s^{-1} , the temperature was between 20 and 160 °C, and the concentrations of the thickener aqueous solutions were 0.3%, 0.4%, 0.5%, 0.6% (mass fraction), respectively, along with a 0.6% guar gum aqueous solution. The rheological properties of different thickeners with temperature changes were evaluated.

The rheological properties of thickeners at different concentrations under multi-level salinity conditions were studied using the Brookfield DV2T viscometer. The experiments were carried out at 120 °C and a shear rate of 170 s^{-1} . The thickener aqueous solutions (0.3%, 0.4%, 0.5%, 0.6%, mass fraction) and a 0.6% guar gum aqueous solution were selected as the base fluids. The influence laws of NaCl (0.0–3.0%) and CaCl_2 (0.0–0.4%) on the solution viscosity were systematically investigated.

2.6. Evaluation of Fracturing Fluid Properties

A HAAKE Mars III HTHP rheometer was employed to assess the shear and temperature resistance properties. The pre-made sample was introduced into the measurement system. Starting from 20 °C, the sample was heated to 170 °C, while continuous shearing was conducted at a shear rate of 170 s^{-1} for 140 min. Based on these monitored data, the rheological stability was evaluated.

The SLSY-1849 fracturing pipeline drag reduction instrument was utilized to assess the efficacy of the fracturing fluid in reducing drag. The pipeline length was 4 m and the inner diameter was 16 mm. In the flow rate range of 100–160 L/min, the pressure differences when clear water and the fracturing fluid passed through the pipeline were measured, respectively. The drag-reduction performance was quantitatively evaluated by comparing the frictional resistance losses of the two at the same flow rate. The following is the calculation formula:

$$DR = \frac{p_1 - p_2}{p_1} \times 100\% \quad (1)$$

In the formula, p_1 represents the frictional pressure difference in the fluid without thickener added, while p_2 represents the frictional pressure difference in the fluid after adding the thickener.

Within a transparent container, 15% (in terms of volume fraction) of ceramsite was evenly distributed in the fracturing fluid under room temperature conditions. After static placement, the sedimentation behavior of the ceramsite was observed and recorded. The static proppant-carrying performance was quantitatively evaluated. This evaluation was conducted by periodically measuring the sedimentation distance of the ceramsite and calculating its sedimentation velocity. The sedimentation velocity is inversely proportional to the proppant-carrying performance.

Ammonium persulfate at a dosage of 0.05 wt% was added to 100 mL of the fracturing fluid as a breaker. After thorough mixing, the fluid was broken for 2 h under specific temperature conditions. After the broken gel fluid was brought to room temperature by cooling, its viscosity was gauged. Subsequently, it was filtered through a $0.8\text{ }\mu\text{m}$ filter membrane. The residue content was ascertained by computing the mass disparity before and after filtration.

3. Results and Discussions

3.1. Structural Characterization of the Thickening Agent

3.1.1. Analysis by FT-IR

The molecular structure of the thickening agent was characterized by infrared spectroscopy, and the results are shown in Figure 3. The vibration absorption of N-H in AM and AMPS is responsible for the intense and wide absorption peaks at 3400 cm^{-1} and 3196 cm^{-1} [20,21]. The peaks in the range of $2912\text{--}2984\text{ cm}^{-1}$ correspond to C-H vibrations, originating from the C-H in AM and the methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) in C16DMAAC [22]. The stretching vibration of the C=O in AM is responsible for the strong absorption peak at 1688 cm^{-1} [23,24]. In contrast, the peak at 1652 cm^{-1} results from the stretching vibration of C=O in NVP [25]. The absorption peaks at 1424 and 1340 cm^{-1} are attributed to the vibrations of $-\text{CH}_2$ and $-\text{C}(\text{CH}_3)_2$, respectively, as indicated in the AMPS model [26]. The absorption peaks at 1340 and 1092 cm^{-1} correspond to the stretching vibrations of C-N in NVP and amide C-N in AM/AMPS, respectively [27]. The stretching vibrations of C-N in NVP are, respectively, associated with the absorption peaks at 1340 cm^{-1} , while the stretching vibrations of amide C-N in AM/AMPS correspond to the absorption peak at 1092 cm^{-1} [28]. The successful copolymerization of AM, AMPS, C16DMAAC, and NVP is verified by the presence of these characteristic absorption peaks.

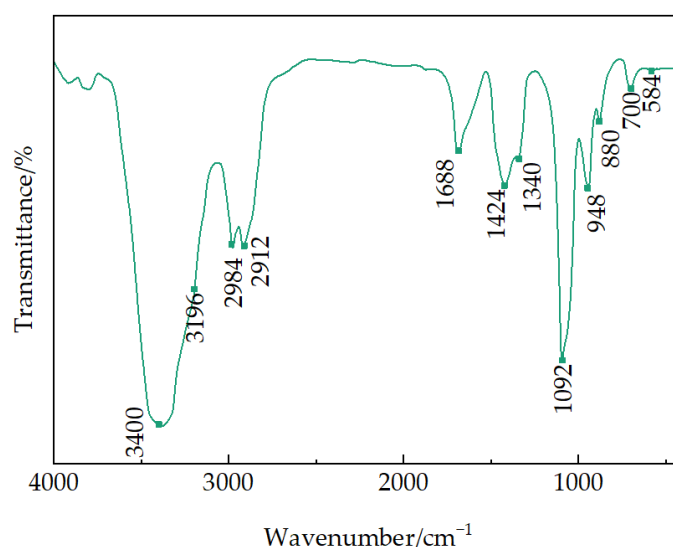


Figure 3. FT-IR of ERT in this study.

3.1.2. Analysis by GPC

The gel permeation chromatography analysis results (Figure 4) exhibited a single characteristic peak, which verified the purity of the target product and the selectivity of the synthesis. The test results indicated that number-average molecular weight (M_n) of this polymer reached 1.13×10^6 , and the weight-average molecular weight (M_w) was 2.36×10^6 , successfully achieving the synthesis of a polymer with a molecular weight in the millions. The dispersity $\bar{D}$ was 2.10, suggesting that the product had a moderate molecular weight distribution.

3.1.3. Analysis by ^1H -Nuclear Magnetic Resonance

Analysis of the ^1H -NMR spectrum (Figure 5) reveals the structural characteristics of the thickening agent. In the low-field area, the proton signal of the terminal $-\text{CH}_3$ in C16DMAAC is observed at $\delta = 0.89\text{ ppm}$. Meanwhile, the intense peak at $\delta = 1.26\text{ ppm}$

can be ascribed to the characteristic absorption of $-(\text{CH}_2)_{15}-$ within its long chain. These two signals clearly confirm the presence of the C16 long chain [29].

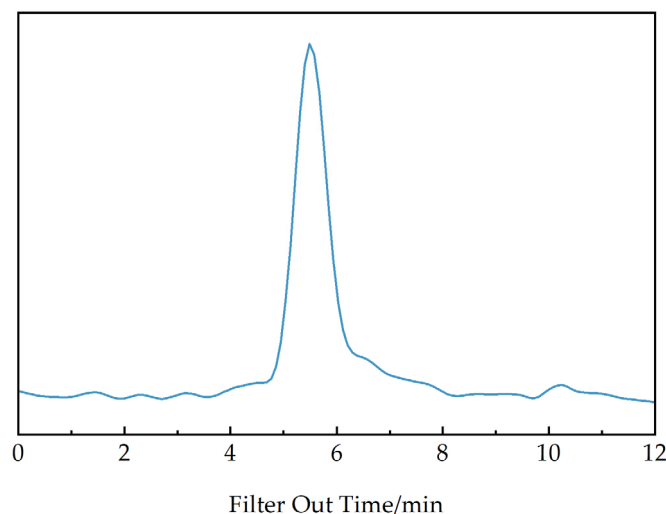


Figure 4. GPC of ERT.

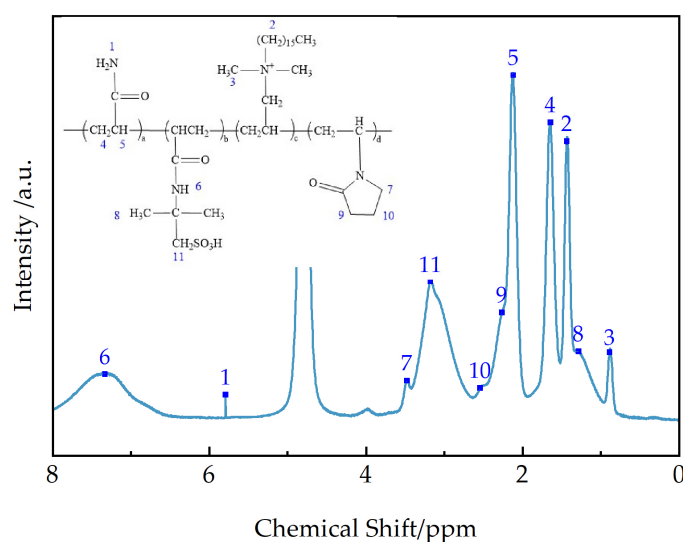


Figure 5. ^1H -NMR Spectrum (D_2O , 25 °C) of ERT.

The proton signals at $\delta = 1.65$ ppm corresponding to $-\text{CH}_2-$ and at $\delta = 2.13$ ppm corresponding to $-\text{CH}-$ confirm the main chain skeleton structure [30]. The successful introduction of AMPS and NVP is verified by the $-\text{CH}_2-$ proton signal at $\delta = 3.19$ ppm and the $-\text{CH}_2-$ proton signals at $\delta = 3.49$ ppm, 2.54 ppm, and 2.27 ppm, respectively [31].

In the high-field area, the characteristic peaks corresponding to $-\text{NH}_2$ of AM and $-\text{NH}-$ of AMPS are observed at $\delta = 5.79$ and 7.32 ppm, respectively. Notably, the characteristic absorption peaks of the $\text{C}=\text{C}$ double bonds in the monomers ($\delta = 6.15$ ppm and $\delta = 4.59$ ppm) completely disappear, indicating that each monomer has fully participated in the polymerization reaction, and the target copolymer structure has been successfully constructed [29].

3.2. Evaluation of the Performance of Thickening Agents

3.2.1. Results of Thermal Stability Evaluation

The thermogravimetric analysis results (Figure 6) indicate that the synthesized thickener exhibits excellent thermal stability. From 40 to 260 °C, there is only a 15% mass loss.

This heat resistance is mainly attributed to the molecular rigidity conferred by the pyrrolidone ring structure in the NVP unit and the long-chain alkyl group of C16DMAAC [32].

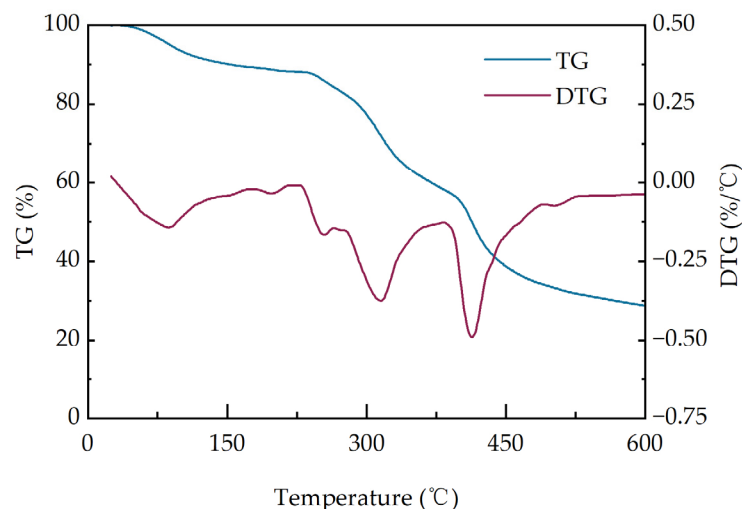


Figure 6. Thermogravimetric analysis curve of ERT.

The thermal degradation process presents five characteristic stages:

- (1) 40–150 °C: The stage of volatilization of surface-adsorbed water and residual small molecules.
- (2) 150–260 °C: The stage of slow weight loss resulting from the gradual decomposition of unstable groups.
- (3) 260–380 °C: The stage of rapid mass loss caused by the deamination reaction of the AM unit and the decomposition of the sulfonic acid group of AMPS.
- (4) 380–460 °C: The stage of the main chain scission of the copolymer.
- (5) 460–600 °C: The stage of slow weight loss, with a final char yield of 25%.

This step-by-step thermal degradation behavior not only reflects the complexity of the copolymer structure but also demonstrates its multi-level thermal stability characteristics. Considering that the temperature of the fracturing reservoir usually does not exceed 200 °C, the thermal stability of this thickener fully meets the requirements of the actual application environment, showing good prospects for engineering applications.

3.2.2. Test Results of Rheological Properties at High Temperatures

The rheological properties of the prepared thickener aqueous solutions at high temperatures were measured. The experimental results (Figure 7) indicate that the rheological behavior of the ERT aqueous solutions exhibits a significant dependence on temperature and concentration. As the concentration of ERT increases from 0.3 wt% to 0.6 wt%, there is a notable rise in the apparent viscosity of the solution. At 20 °C, the viscosities of ERT solutions with different concentrations are 74.93 mPa·s, 89.75 mPa·s, 99.04 mPa·s, and 113.45 mPa·s, respectively, suggesting that the network structure among ERT molecules gradually strengthens.

Nevertheless, when the concentration is relatively high (≥ 0.5 wt%), within the temperature range of 50–80 °C, a notable thermosensitive thickening phenomenon takes place. Specifically, the viscosity of the 0.6 wt% ERT solution increases from 115.13 mPa·s to 122.43 mPa·s, and that of the 0.5 wt% solution increases from 105.63 mPa·s to 112.74 mPa·s. This phenomenon is attributed to the conformational changes in ERT molecules within a specific temperature range, which enhance the intermolecular hydrophobic association [33] and form a more compact network structure.

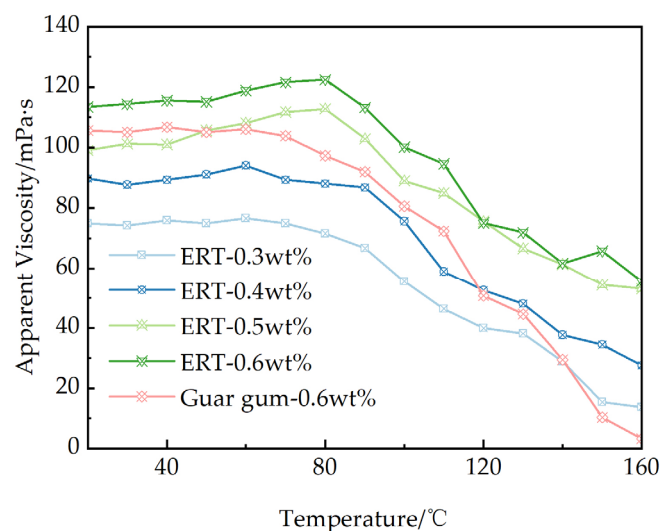


Figure 7. Temperature-viscosity curves of ERT solutions at various concentrations.

The structures of the thickener at different concentrations within the temperature range from 50 to 80 °C are presented in Figure 8. When the ERT concentration ≤ 0.4 wt%, with the increase in temperature, the main chain of ERT unfolds due to molecular thermal motion. This inhibits effective interaction among the hydrophobic groups in C16DMAAC, leading to a reduction in viscosity as the temperature rises. When the concentration ≥ 0.5 wt%, as the temperature rises, the structure of the molecular chains becomes more compact, and the association between hydrophobic groups is enhanced, thus leading to an increase in solution viscosity.

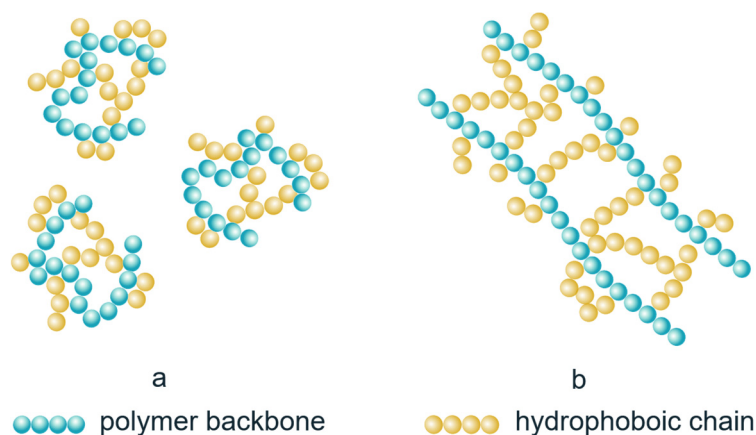


Figure 8. Schematic structure of thickener at different concentrations. (a) ERT concentration ≤ 0.4 wt%. (b) ERT concentration ≥ 0.5 wt%.

The thermosensitive thickening characteristics exhibited by ERT solutions essentially stem from the complex and diverse interaction mechanisms within the polymer chains. At low concentrations (≤ 0.4 wt%), from a microscopic perspective, the hydrophobic groups contained in C16DMAAC mainly tend to undergo internal association (Figure 8a). Temperature is a crucial influencing factor. As the temperature gradually increases, the energy obtained by the molecular system increases, and the thermal motion of molecular chains is significantly enhanced [17]. The intensification of this thermal motion interferes with and weakens the original intermolecular interactions. A decrease in intermolecular interactions directly results in a reduction in solution viscosity. When the solution concentration reaches a relatively high level (≥ 0.5 wt%), the interaction mode within the system changes

significantly. At this time, the hydrophobic groups of C16DMAAC, through the hydrophobic effect, undergo more external association (Figure 8b). This external association acts like building bridges, connecting each molecule to gradually construct a more stable three-dimensional network structure [34]. With a further increase in temperature, this three-dimensional network structure not only remains intact but even becomes more stable due to the further adjustment and consolidation of the structure by molecular thermal motion, thus strongly supporting the increase in solution viscosity.

In addition, $-\text{SO}_3\text{H}$ in AMPS and $-\text{CONH}_2$ in AM play roles in intermolecular electrostatic stabilization and hydrogen bonding. Especially at higher concentrations, the strong electronegativity and hydrogen bonding of sulfonic acid groups in water enhance the intermolecular network connectivity, enabling the ERT solution to better maintain its structural stability and thickening effect at high temperatures [35]. NVP, by regulating the hydrophilicity and flexibility of ERT, promotes temperature-induced structural changes, thus further enhancing the thermosensitive thickening performance.

In comparison with guar gum, ERT exhibits more excellent thickening performance under high-temperature conditions. When the temperature exceeds $80\text{ }^\circ\text{C}$, the viscosity of the guar gum solution decreases sharply. This phenomenon is particularly pronounced at $120\text{ }^\circ\text{C}$, where the viscosity of a $0.6\text{ wt}\%$ guar gum solution declines to $50.72\text{ mPa}\cdot\text{s}$. Nevertheless, at identical temperature settings, the viscosity of the ERT solution stays at a level higher than $75.01\text{ mPa}\cdot\text{s}$. This indicates that ERT has stronger molecular network stability and anti-degradation ability in a high-temperature environment and can maintain its thickening effect at higher temperatures.

3.2.3. Test Results of Salt Resistance

The apparent viscosity of ERT under different inorganic salt concentrations was measured. The research results (Figure 9) indicate that NVP exhibits excellent functional characteristics in the ERT system. Through its unique lactam structure, it significantly enhances the hydrophilicity of the polymer and provides good salt resistance stability. ERT shows excellent salt tolerance under various salinity conditions, especially in low salinity environments ($\text{NaCl} < 2.0\%$, $\text{CaCl}_2 < 0.2\%$). Even under higher salt concentration conditions, ERT can still maintain ideal rheological properties.

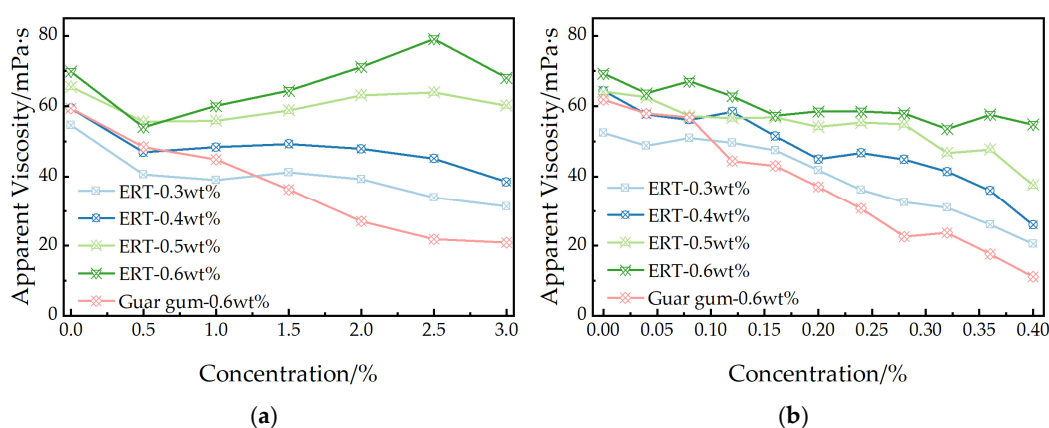


Figure 9. Variations in the apparent viscosity of thickening agents with the concentration of inorganic salts. (a) NaCl solutions. (b) CaCl_2 solutions.

A comparative analysis shows that ERT has significant performance advantages over traditional guar gum. In high salinity environments, especially in the presence of Ca^{2+} , ERT demonstrates remarkable stability. For example, in a $0.4\text{ wt}\%$ CaCl_2 environment, a $0.6\text{ wt}\%$ ERT solution can still maintain a high viscosity level of $54.75\text{ mPa}\cdot\text{s}$, while the viscosity of

the guar gum solution drops to 11.14 mPa·s. This excellent performance stems from the unique molecular structure design of ERT. AMPS's sulfonic acid groups are responsible for its outstanding salt tolerance [36]. The hydrophobic association mediated by C16DMAAC provides strong stability support for the molecular network, and the introduction of NVP further optimizes the water solubility of the system. This multiple synergy makes ERT a new type of thickener with outstanding performance and significant application advantages under complex formation conditions with high concentrations of inorganic salts.

3.3. Performance Evaluation of Fracturing Fluids

3.3.1. Test Results of Shear and Temperature Resistance Performance

As depicted in Figure 10, in order to assess the shear and temperature resistance of the fracturing fluid with 0.6% thickener, the rheological characteristics of this fluid were measured for a 140 min duration at 170 °C. During the experiment's initial phase (lasting from 0 to 12 min), as the temperature rose to 80 °C, the viscosity stayed above 100 mPa·s. It attained a peak value of 165.75 mPa·s at the 8 min mark. This indicates that the system can still maintain a high viscosity during the heating process, with a relatively stable molecular chain structure, demonstrating good temperature resistance.

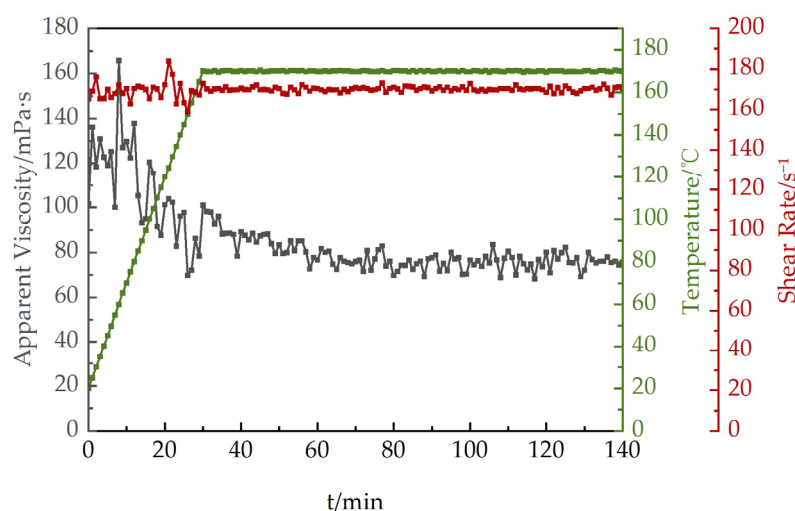


Figure 10. Curves of Shear and Temperature Resistance Performance of Fracturing Fluid Containing 0.6wt% ERT.

Over the following 12–30 min, the temperature of the fracturing fluid kept increasing until it reached 170 °C. Meanwhile, the viscosity exhibited a slightly declining tendency yet still stayed within the range of 70–120 mPa·s. This indicates that the system can still maintain strong rheological stability under high-temperature conditions, without obvious molecular degradation. After 30 min, the system entered a viscosity-stable stage. The temperature was maintained at 170 °C, and the viscosity fluctuated in the range of 68–98 mPa·s, with relatively small overall changes. This shows that the molecular structure of the thickener still has good stability under high-temperature and high-shear conditions. This characteristic enables the fracturing fluid to have enough proppant-carrying capacity within the high-temperature environment of deep wells. As a result, proppants can be smoothly transported to the deep sections of fractures, enhancing the effectiveness of fracturing operations.

3.3.2. Test Results of Drag Reduction Performance

To assess the adaptability of the fracturing fluid under diverse flow rate conditions, its drag reduction performance was examined within a flow rate range from 110 to 150 L/min.

The results are presented in Figure 11. Experimental findings suggest that as the flow rate rises, the drag reduction rate typically exhibits an upward tendency. This demonstrates that the system can effectively reduce the turbulent resistance in pipelines at higher flow rates, thereby decreasing the pumping pressure and enhancing construction efficiency.

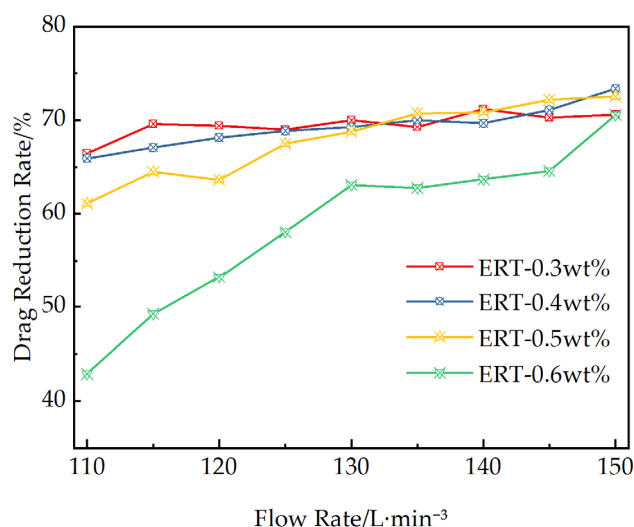


Figure 11. Graph depicting how the drag reduction rate of fracturing fluids having various ERT concentrations varies with the flow rate.

Specifically, when the flow rate increases from 110 L/min to 150 L/min, the drag reduction rate of ERT0.3 (fracturing fluid containing 0.3 wt% thickener) slightly rises from 66.44% to 70.60%, demonstrating relatively stable drag reduction ability. The drag reduction rate of ERT0.4 increases from 65.92% to 73.38%, with a more significant increase. The drag reduction rate of ERT0.5 increases from 61.11% to 72.56%, indicating that the drag reduction effect at this concentration improves significantly with the increase in the flow rate. While the drag reduction rate of ERT0.6 surges from 42.90% to 70.56%, suggesting that the drag reduction performance of the high-concentration thickener is more dependent on the flow rate.

The above trends can be attributed to the enhanced turbulence caused by the increase in flow rate, which makes the orientation effect of polymer chains more prominent under high-speed flow, thus reducing the formation of turbulent eddies and improving the drag reduction efficiency [37,38]. Furthermore, regarding the alterations in the drag reduction rates of solutions with varying concentrations, the drag reduction rates of ERT0.3 and ERT0.4 achieve a relatively high level at lower flow velocities. As the flow velocity rises, they exhibit a trend of slow growth. Nevertheless, in the initial phase, ERT0.6 has a relatively low drag reduction rate, yet this rate rises notably as the flow rate goes up. This indicates that the high-concentration solution has more outstanding drag reduction ability at high flow rates.

Analysis indicates that this thickening agent can maintain excellent drag-reduction performance within a wide range of flow rates. Notably, under high-flow conditions, it can significantly reduce the transportation resistance of fracturing fluid. This is conducive to reducing pumping energy consumption and enhancing the efficiency of fracturing operations.

3.3.3. Test Results of Static Sand-Carrying Performance

This study systematically investigated the impact of temperature on the proppant-carrying capacity of ERT fracturing fluids at different concentrations and guar gum fracturing fluids. As depicted in Figure 12, the experimental findings indicated that when the

temperature rose from 30 °C to 150 °C, an upward tendency was exhibited in the overall sedimentation rate of ceramsite within the fracturing fluids. This was mainly because the enhanced molecular thermal motion caused by the temperature rise weakened the intermolecular forces, thus reducing the viscosity of the fracturing fluids.

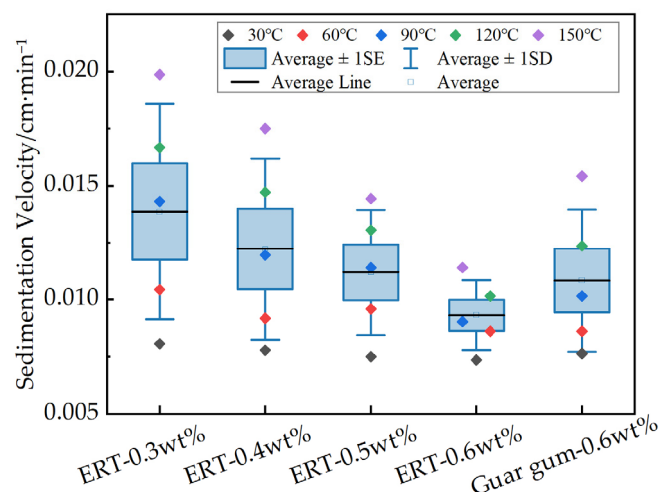


Figure 12. Graph of the sedimentation rate of fracturing fluids in systems composed of different gelling agents under various temperature working conditions.

Specific analysis revealed that at 30 °C, the sedimentation rate of ceramsite ranged from 7.36×10^{-3} – 8.06×10^{-3} cm/min (ERT concentration of 0.3–0.6 wt%), while that of 0.6 wt% guar gum fracturing fluid was 7.64×10^{-3} cm/min. As the temperature elevated to 150 °C, the sedimentation rate of ERT fracturing fluids at various concentrations increased to 1.139×10^{-2} – 1.986×10^{-2} cm/min, and that of the 0.6 wt% guar gum fracturing fluid increased to 1.542×10^{-2} cm/min.

Significantly, the sedimentation rate was notably influenced by the concentration of ERT. Taking 150 °C as an example, when ERT concentration increased from 0.3 wt% to 0.6 wt%, sedimentation rate decreased from 1.986×10^{-2} cm/min to 1.139×10^{-2} cm/min, with a decrease of 42.6%. This was because a higher polymer concentration not only provided more thickening groups but also strengthened the hydrophobic association between molecules, forming a more stable network structure.

When comparing ERT and guar gum fracturing fluids with the same concentration (0.6 wt%), the ERT system exhibited a lower sedimentation rate at each temperature point. Especially in the high-temperature region, the advantage of ERT was more prominent. At 150 °C, the sedimentation rate of 0.6 wt% ERT fracturing fluid, which was (1.139×10^{-2} cm/min), showed a 26.1% decrease compared to that of guar gum fracturing fluid, with a value of (1.542×10^{-2} cm/min). This excellent high-temperature performance mainly benefited from the temperature-resistant structures of AMPS and NVP monomers and the temperature-responsive hydrophobic association mediated by C16DMAAC.

From the perspective of molecular interaction mechanisms, as the temperature increased, the hydrophobic groups in ERT molecules (mainly from C16DMAAC) underwent stronger hydrophobic association, partially offsetting the viscosity decrease caused by the temperature rise. Meanwhile, the sulfonic acid groups of AMPS and the cyclic structure of NVP could stabilize the molecular conformation and maintain the viscoelasticity of the solution [39]. This explained why high-concentration ERT fracturing fluids showed better temperature stability, and the sensitivity of their sedimentation rate to temperature changes was significantly reduced.

Overall, under all test conditions, the sedimentation rate of ceramsite in ERT fracturing fluids did not exceed the critical value of 2×10^{-2} cm/min, fully demonstrating the effectiveness of the synergistic design of multifunctional monomers. Each functional unit in the ERT molecular structure, through different action mechanisms, jointly ensured that the fracturing fluid could still maintain excellent proppant-carrying capacity under high-temperature conditions, ensuring a uniform distribution of proppants in the fractures and thus effectively enhancing the fracturing stimulation effect.

3.3.4. Gel-Breaking Performance Test Results

As presented in Table 3, the experimental outcomes reveal that, across various temperature conditions, the ERT and the traditional guar gum fracturing fluid both demonstrate outstanding gel-breaking capabilities. Within the temperature range, the viscosities in the two fracturing fluid systems show a significant decreasing trend. The ERT fracturing fluid shows a decrease in viscosity, from 4.8 mPa·s to 3.8 mPa·s. Meanwhile, the guar gum fracturing fluid experiences a drop in viscosity, from 4.7 mPa·s to 3.6 mPa·s. This indicates an ideal gel-breaking effect.

Table 3. Fracturing Fluid Gum Breaking Performance Test Results.

Temperature	The Gel-Breaking Fluid's Viscosity/mPa·s		Content of Residues/mg·L ⁻¹		The Gel-Breaking Fluid's Variable Tension/mN·m ⁻¹		The Gel-Breaking Fluid's Interfacial Tension/mN·m ⁻¹	
	ERT	Guar Gum	ERT	Guar Gum	ERT	Guar Gum	ERT	Guar Gum
60 °C	4.8	4.7	165.3	215.5	23.65	24.35	1.02	1.12
90 °C	4.3	4.2	159.6	195.3	22.15	22.35	0.95	1.09
120 °C	3.8	3.6	146.7	185.6	21.65	21.65	0.84	0.95

The assessment of gel-breaking performance in fracturing fluids necessitates the consideration of residue content, which serves as a critical metric. The data indicate that, at every temperature point, the residue content of the ERT fracturing fluid is considerably lower compared to that of the guar gum system. At 60 °C, the residue content of ERT is 165.3 mg·L⁻¹, which is 23.3% lower than that of guar gum (215.5 mg·L⁻¹). Even under the high-temperature condition of 120 °C, the ERT system still maintains a relatively low residue content (146.7 mg·L⁻¹), which is 21.0% lower than that of the guar gum system (185.6 mg·L⁻¹). This outcome suggests that the ERT fracturing fluid exhibits enhanced degradability, thereby mitigating the potential for reservoir blockage and preserving formation permeability.

The veracity of the ERT fracturing fluid's exceptional performance is substantiated by the empirical evidence derived from the interfacial and surface tension tests. With the increase in temperature, the surface tensions of both systems show a downward trend, but the surface tension of the ERT fracturing fluid (23.65–21.65 mN·m⁻¹) at each temperature point is lower than or equal to that of the guar gum system (24.35–21.65 mN·m⁻¹). Meanwhile, the ERT fracturing fluid also exhibits a lower interfacial tension, decreasing from 1.02 mN·m⁻¹ at 60 °C to 0.84 mN·m⁻¹ at 120 °C, all of which are lower than the corresponding values of the guar gum system at the same temperatures (1.12–0.95 mN·m⁻¹). The introduction of the C16DMAAC monomer is responsible for this outstanding surface/interfacial property. This introduction is advantageous for enhancing the recovery efficiency of the gel-broken fluid and the cleanliness of the reservoir.

A thorough examination of the molecular structure design of ERT fracturing fluid reveals its exceptional gel-breaking performance. Firstly, the introduction of the C16DMAAC monomer not only endows the system with good surface activity but also its long-chain structure is easy to break during the gel-breaking process, which helps to accelerate the

degradation of molecular chains. Secondly, although the AMPS and NVP monomers provide temperature stability, their side groups can undergo directional cleavage under the action of the gel-breaker, forming low-molecular-weight fragments and promoting the gel-breaking process. Finally, the multi-functional structure of the copolymer shows a synergistic degradation effect under the action of the gel-breaker. The step-by-step cleavage of each functional group ensures the integrity of the degradation process and minimizes the generation of insoluble residues. This structure-oriented degradation mechanism enables the ERT fracturing fluid to achieve rapid and complete degradation during the gel-breaking stage, avoiding reservoir pollution.

4. Conclusions

In this study, an environmentally responsive thickener for shale gas reservoir fracturing fluids was successfully developed. Four functional monomers, namely AM, AMPS, C16DMAAC, and NVP, were copolymerized via aqueous solution free radical polymerization. The following conclusions were reached by means of systematic structural characterization and performance evaluation:

(1) The optimal preparation process parameters of the thickener were determined through orthogonal experiments. The mass fraction of the initiator was 0.3%, the reaction pH was 6.5, and the temperature was set at 60 °C. The total mass fraction of monomers amounted to 25%, with the four monomers AM, AMPS, C16DMAAC, and NVP having a mass ratio of 15:10:3:2.

(2) The utilization of an array of characterization techniques has led to the substantiation of the effective synthesis of the target product, thereby affirming its exceptional properties. The results of FT-IR and ¹H-NMR verified the formation of the expected molecular structure. GPC testing showed that M_n reached 1.13×10^6 , the M_w was 2.36×10^6 , and the dispersity ($\bar{D}$) was 2.10. TGA analysis indicated that the product had excellent thermal stability, with a mass loss of only 15% in the temperature range of 40–260 °C, fully meeting the temperature environmental requirements of shale gas reservoirs.

(3) The evaluation results of environmental response performance showed that when the ERT concentration was $\geq 0.5\%$, the thickener exhibited a significant thermosensitive thickening effect, with a viscosity increase of more than 49% compared to the control group at 120 °C. It maintained a high viscosity of 54.75 mPa·s in a 0.4 wt% CaCl₂ environment, 46.61 mPa·s higher than the control group, demonstrating excellent salt resistance.

(4) The evaluation results of the fracturing fluid's comprehensive performance demonstrated the following: when subjected to the harsh conditions of 170 °C and a shear rate of 170 s^{−1} for 140 min, the viscosity stayed above 68 mPa·s, which indicates outstanding shear and temperature resistance. In the flow rate range of 110–150 L/min, a significant drag-reduction effect was observed, with a maximum drag-reduction rate of 70% being attained. It possessed excellent static sand-carrying performance, as the ceramsite settlement rate was merely 2×10^{-2} cm/min. It was discovered that the residue content after gel-breaking was below 165.3 mg/L, while the viscosity of the gel-broken fluid did not go beyond 4.8 mPa·s. All these aspects fully satisfy the technical requirements for low-damage fracturing fluids in shale gas reservoir stimulation.

The environmentally responsive fracturing fluid thickener developed in this paper exhibits stable viscosity at 150 °C and has a significant drag reduction effect, which is suitable for enhanced geothermal systems to a certain extent and has potential for application. However, the formation environment of enhanced geothermal systems is more complex, and the fracturing fluid needs to withstand higher temperatures and special chemical environments. In the future, we need to further study the adaptability of this thickener in high temperatures exceeding 300 °C and special geothermal environments,

and through optimizing the formulation and process, it is expected that it can be extended to the reservoir modification of other underground energy systems, such as enhanced geothermal systems, so as to provide broader support for energy extraction.

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