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Synthesis and application of nonionic polyacrylamide with controlled molecular weight for fracturing in low permeability oil reservoirs

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ABSTRACT: Nonionic polyacrylamide (NPAM) with controlled molecular weight was successfully synthesized as a gel fracturing fluid by aqueous solution polymerization. The effects of the monomer concentration, initiator concentration, reaction time, feeding temperature and reaction temperature on the molecular weight were systematically investigated through single-factor and orthogonal experiments. The NPAM molecular weight can be controlled by adjusting these factors. The decisive factor is the acrylamide concentration, whereas the initiator concentration and feeding temperature are secondary factors. These synthetic NPAMs can be crosslinked with zirconium acetate to produce a gel fracturing fluid for use in low permeability oil reservoirs. Gel fracturing fluids based on synthetic NPAMs have high shear resistance, low filtration performance, easy gel breaking performance, good proppant carrying capability and low core damage capability. By adjusting the NPAM or crosslinker concentrations, the gel fracturing fluid can be adapted for use in low permeability oil reservoirs for a wide temperature range $(60-120^{\circ}C)$. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41637.

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INTRODUCTION

Hydraulic fracturing technology is widely used to recover oil from low permeability reservoirs.¹⁻⁵ In the hydraulic fracturing process, a fracturing fluid is injected through a wellbore and against the face of the formation at high pressures; subsequently, the formation is forced to crack and fracture. The whole process is completed within 3 h. The fracturing fluid usually carries a proppant, such as 20-40 mesh sand, ceramics, or glass beads, which is suspended in the fracturing fluid and is transported into the fracture. The proppant prevents the fracture from closing and thus provides an improved flow of the recoverable fluid, i.e., oil, gas, or water.^{6,7} Therefore, the fracturing fluid is a critical component for a successful hydraulic fracturing treatment. In recent years, a wide variety of fluids, such as gelled, foamed, and viscoelastic surfactant fluids, have been developed. However, most gelled fluids based on guar are limited by their high costs and high residual contents, which typically result in formation damage, especially when fluids with high guar concentrations are used in high-temperature wells.^{8,9} In high-temperature or ultra-deep wells, foamed and viscoelastic surfactant fluids have low viscosities and cannot effectively transport proppant without the use of a crosslinker, resulting in treatment failures.10-12

To overcome these problems, gelled fluids based on synthetic polymers with good proppant transport properties, shear and high temperature resistance, low fluid loss properties, and good cleanup properties have been studied. Generally, low-cost zirco-nium crosslinked polymer gel fluids with lower toxicity are used in low permeability reservoirs. However, these studies have primarily focused on low-temperature formations;¹³ therefore, these observations may not be applicable for ultra-deep wells and high-temperature reservoirs. To overcome these issues, an environmentally friendly polymer gel fracturing fluid based on zirconium acetate is proposed; this fluid provides excellent proppant transport capabilities at temperatures as high as 200°F. However, there are very few polymers available for use in gel fracturing fluid, which limits their applications in the oilfield.

Polymers are generally subdivided into three categories: anionic, cationic, and nonionic. Cationic polymers are primarily used as clay stabilizers and flocculants in the petroleum industry. Anionic polymers are typically used for profile control and water shutoff in mature oilfields.^{14–16} Previous studies have shown that these two polymers can be crosslinked by organic or inorganic crosslinkers.¹⁷ However, in those studies, the crosslinking gelation time was too long and proppants could not be

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transported into formations within 3 h. These two polymer categories are not suitable for gel fracturing fluids. Fortunately, treatments with nonionic polymers have been successful in the fracturing of low permeability oil reservoirs. However, nonionic polymers are associated with high costs and complex synthesis methods which further limit their applications in fracturing treatments. Therefore, it is necessary to provide a simple method for the synthesis of nonionic polymers. In general, four synthetic methods, i.e., aqueous solution polymerization, inverse emulsion, suspended polymerization, and radiation polymerization, are used for the synthesis of the polymers. Hydrophobic water-soluble polymers were synthesized using inverse emulsion polymerization. However, a significant amount of organic solvents were required, which increases the production cost and complexity.^{18,19} For the suspended polymerization method, the produced synthetic polymer has a narrow molecular weight range and cannot effectively react with zirconium acetate.²⁰ The radiation polymerization method has a low energy consumption and a high-purity quotient, but presented difficulties in forming polymers with high molecular weights and sufficient degrees of polymerization.²¹ The aqueous solution polymerization method offers a simple process and a low cost;^{22,23} herein, we describe the synthesis of nonionic polymers with controlled molecular weights by this method.

The focus of the present study was the synthesis of nonionic polyacrylamide (NPAM) with different molecular weights using the aqueous solution polymerization method. We primarily studied factors that influence NPAM synthesis. The monomer concentration, initiator concentration, reaction time, feeding temperature, and reaction temperature were investigated, and the performance of gel fracturing fluids based on synthetic NPAMs was evaluated in detail. The results of this study may serve as a reference for understanding the synthesis of NPAM. Through additional experiments, we expect that this work can be further promoted and be applied in gel fracturing treatments in low permeability oil reservoirs.

MATERIALS AND METHODS

Materials

An acrylamide monomer (AM) was obtained from Jiangxi Agriculture Chemical, China. Analytical-reagent grade ammonium persulfate (APS) was provided by Guo Guang, China. Methyl orange, methyl red, indigo carmine, bromocresol green, anhydrous sodium carbonate, and hydrochloric acid were chromatographically pure. Double-distilled water was used for the preparation of nonionic polymers.

Synthesis of Nonionic Polymer

Synthesis experiments were conducted using a three-neck flask placed in a thermostated water bath. The typical synthesis was as follows: 80 mL of double-distilled water and 0.8 g of AM were added to a 150-mL three-neck flask equipped with a mechanical stirrer. The solution was stirred under nitrogen until uniform dispersion. During stirring, 0.08 g of APS was added into the solution. The mixture was then stirred continuously under nitrogen at the feeding temperature of 53° C for 10 min. Then, the reaction was initiated at 60° C for 3 h. The nonionic polymer was collected and washed alternatively with double-distilled

water and methanol, and subsequently dried in a vacuum oven at 60°C for 24 h. The obtained white particles were the final NPAM products. The polymerization process of AM is demonstrated below:

nCH₂=CH-
$$\overset{O}{C}$$
-NH₂ $\xrightarrow{\text{initiator}}$ -{CH₂-CH}_n
O=C-NH₂

Determination of Molecular Weight

The molecular weight of synthetic NPAM was determined according to the Chinese Oil and Gas Industry Standards of GB/T 12005.10-92-"Determination for molecular weight of polyacrylamide by viscometry."²⁴

Performance of Gel Fracturing Fluid Based on Synthesis Nonionic Polymer

The gelation time, shear resistance, filtration performance, gel breaking performance, sand-carrying capability, and core damage capability were investigated according to the Chinese Oil and Gas Industry Standards of SY/T 6376-2008 "General technical specifications of fracturing fluids."²⁵

RESULTS AND DISCUSSION

Synthesis of NPAM

Effect of AM Concentration. To study the effect of AM concentration on the molecular weight of synthetic NPAM, single-factor experiments were conducted. The AM concentration was varied from 4 to 19%, whereas the initiator concentration was maintained at 0.01%, the reaction time was 4 h, and the feeding and reaction temperatures were 56 and 62°C, respectively.

Figure 1 shows the variation of molecular weight versus AM concentration. The molecular weight sharply increases as the AM concentration increases and reaches a maximum value when the AM concentration is 16%. However, the molecular weight declines when adding AM concentrations above 16%. Generally, a polymer increases its chain length during the polymerization process. The lower AM concentration has lower polymerization rates between AM molecules, which reduces the



Figure 1. Effect of AM concentration on molecular weight.



overall reaction rate. It is difficult to completely polymerize the solution in a short time. Additionally, the lower AM concentrations do not provide sufficient molecular numbers for the formation of long chain reactions. As a consequence, the average molecular weights of the resultant polymer solutions are relatively low. In general, the average molecular weight increases as the AM concentration increases. However, the average molecular weight decreases when the AM concentration exceeds a certain value limit. Because the polymerization is an exothermic process, the reaction temperature will sharply rise when the AM concentration increases. Large quantities of reaction heat are difficult to disperse and result in faster initiation processes and chain transfer reactions, which can lead to molecular chain cleavage and subsequently, lower molecular weights. Moreover, because higher AM concentrations result in higher system temperatures, imidization reactions occur between NPAM chains resulting in decreases in their molecular weights.

Effect of Initiator Concentration. Single-factor experiments were conducted to investigate the effect of initiator concentration on the molecular weight. The initiator concentration varied from 0.001 to 0.04%, whereas the AM concentration was fixed at 16%, the reaction time was fixed at 4 h, and the initiator feeding temperature and reaction temperature were 56 and 62°C, respectively. As shown in Figure 2, the molecular weight of NPAM increases with the initiator concentration. When the initiator concentration increases to 0.007%, the molecular weight reaches a maximum. However, the molecular weight decreases at higher initiator concentration. During the polymerization process, the initiator is considered the activity center of radical polymerization. When the initiator concentration is low, the initiator is surrounded by AM or solvent, which decreases the rate of radical polymerization, resulting in low molecular weight. As the initiator concentration increases, the activity center also increases, leading to rapid polymerization and early termination and thereby, high molecular weight formation. When the initiator amount exceeds a certain value limit, excessive initiators causes the oxidative degradation of NPAM and the subsequent formation of short molecular chains. As a result, the average molecular weight remains low for high initiator concentrations.



Figure 2. Effect of initiator concentration on molecular weight.



Figure 3. Effect of reaction time on molecular weight.

Effect of Reaction Time. Experiments were performed as follows. The AM and initiator concentrations were, respectively, fixed at 16 and 0.007%, whereas the feeding and reaction temperatures were, respectively, set at 56°C was 62°C. Figure 3 shows the effect of the reaction time on the molecular weight. In Figure 3, the molecular weight reaches a maximum when the reaction time increases to 4 h, but the molecular weight decreases for longer reaction times. When the reaction time is less than 4 h, the polymerization is not complete, leading to low molecular weight. When the reaction time is longer than 4 h, the molecular weight sharply decreases. This is likely due to the decreasing amount of reactants, which decreases the polymerization rate. Additionally, APS degrades both accelerators and initiators; as such, NPAM degradation continues during the polymerization process. When the reaction time exceeds 4 h, the degradation rate may be greater than the polymerization rate, resulting in a lower molecular weight.

Effect of Initiator Feeding Temperature. To study variable feeding temperatures, experiments were fixed at 16% AM and 0.007% initiator concentrations, at 4 h reaction time and at 62°C reaction temperature. As shown in Figure 4, for increasing feeding temperature, the molecular weight initially rapidly increases until a maximum, then slightly decreases. When the



Figure 4. Effect of initiator feeding temperature on molecular weight.



Figure 5. Effect of reaction temperature on molecular weight.

feeding temperature is lower than the polymerization temperature, persulfate radical ions are formed by thermal decompositions, which are considered first order reactions.²⁶ During this process, new monomer radicals are generated as sulfate ion radicals impact AM molecules. For the 62°C reaction temperature, most monomer radicals have sufficient activation energy for polymerization reactions to occur. Because the life expectancy of a radical is 10^{-9} to 10^{-11} s at lower feeding temperatures,²⁷ an effective monomer radical directly copolymerizes in the reaction. However, fewer monomer radical are effective at lower feeding temperatures, which further affects polymerizations. As the feeding temperature increases above 52° C, excessive free radicals involved in the reaction generate, resulting in the for-

Table I. The Factors and Levels of the Pyrolysis System

Factor code	Factors	Levels
А	AM concentration (%)	A1 10
		A2 13
		A3 16
		A4 19
В	Initiator concentration (%)	B1 0.0045
		B2 0.0070
		B3 0.0095
		B4 0.012
С	Feeding temperature (°C)	C1 47
		C2 50
		C3 53
		C4 56
D	Reaction temperature (°C)	D1 56
		D2 59
		D3 62
		D4 65
E	Reaction time (h)	E1 2
		E2 3
		E3 4
		E4 5

		Levels				Molecular	
No.	А	В	С	D	Е	(10 ⁴ g/mol)	
1	1	1	1	1	1	549.26	
2	1	2	2	2	2	602.32	
3	1	З	З	3	3	666.38	
4	1	4	4	4	4	620.27	
5	2	1	2	З	4	680.38	
6	2	2	1	4	З	720.42	
7	2	З	4	1	2	691.22	
8	2	4	З	2	1	664.86	
9	З	1	З	4	2	756.83	
10	З	2	4	З	1	817.58	
11	З	З	1	2	4	757.35	
12	З	4	2	1	З	646.91	
13	4	1	4	2	З	724.35	
14	4	2	З	1	4	797.90	
15	4	З	2	4	1	719.40	
16	4	4	1	З	2	735.86	

Table II. Analyses of Orthogonal Experiments

mation of short molecular chain NPAMs with low molecular weights.

Effect of Reaction Temperature. To study the effect of the reaction temperature, experiments were conducted at a constant 16% AM, 0.007% initiator concentration, 52°C feeding temperature, and 4-h reaction time. Figure 5 shows the changes in the molecular weight with respect to the reaction temperature. The molecular weight increases as the reaction temperature initially increases but decreases when the reaction temperature rises above 62°C. It is likely that the activation energy of AM radicals is lower at low reaction temperatures, resulting in short molecular chains. As the reaction temperature rises above 62°C, most radicals have sufficient activation energy to initiate polymerization. However, at higher reaction temperatures, the chain transfer rate is greater than the chain propagation rate. As a result, the radical end of the polymerized chain undergoes a chain transfer reaction to the inhibitor, thereby terminating the chain and leading to shorter chains. Additionally, oxidative degradation can occur at high temperatures, further reducing the molecular weight.

Brief Analysis of Orthogonal Experiments. Based on the previously discussed single factor experiments, orthogonally designed experiments of five factors and four levels were adopted to optimize the synthesis conditions. The results are shown in Tables I–III. The results indicate that AM functions as the building block for polymerizations, and the initiator concentration and feeding temperature are secondary factors that determine the molecular weight of NPAM. Other components, such as reaction time and reaction temperature, also affect the polymerization rate and features of NPAM.



		Molecular weight (10 ⁴ g/mol)				
	A	В	С	D	E	
K ₁ K ₂	2438.23 2756.88	2710.82 2938.22	2762.89 2649.01	2685.29 2822.43	2751.10 2786.23	
Кз	2981.67	2834.35	2885.97	2900.20	2758.06	
K ₄	2977.51	2667.90	2853.42	2816.92	2855.90	
k1	609.56	677.71	690.72	671.32	687.78	
k ₂	689.22	734.56	662.25	705.61	696.56	
k ₃	745.42	708.59	721.49	725.05	689.52	
k ₄	744.38	666.98	713.36	704.23	713.98	
$R = k_{i \max} - k_{i \min}$	135.86	67.58	59.24	53.73	26.20	

Table III. Effects of Various Factors on Molecular Weight

Remark: K_i refers to the sum of the quality indicators of all *i* factors; k_i is the average of K_i ; *R* is the range of the indicator and is calculated from the difference between the maximum and minimum values of k_i .

Characterization of NPAM

The Fourier transform infrared (FTIR) spectrometer of the synthesized polymers was determined using a FTIR spectrophotometer (Nicolet Nexus 470, NICOLET). In this study, NPAM used as the crosslinked gel fracturing fluid and was synthesized with 16% AM and 0.01% initiator concentrations at a feeding temperature of 52°C and a reaction temperature of 62°C for 4 h; the resultant molecular weight was 6,648,600 g/mol. The purified polymers were ground with potassium bromide (KBr) powder and pressed into pellets for FTIR measurement at a frequency range of 400–4000 cm^{-1} . The results are illustrated in Figure 6. The broader bands at 3430 cm⁻¹ were caused by the stretching of hydroxyl groups. The bands at 2920 and 2850 cm⁻¹ were due to stretching vibration peaks of -CH₃ and -CH₂. Peak at 1630 cm⁻¹ in FTIR spectrometer could be ascribed to the stretching of carboxylate anions groups (i.e., -COO⁻), indicating that -COO⁻ was formed after the aqueous solution polymerization reaction. When the NPAM reacts with zirconium acetate, the reaction between the carboxylate group (-COO-) and Zr (IV)-ligand can easily take place,²⁸ forming a gel fracturing fluid.





Performance Evaluation of Gel Fracturing Fluid

The NPAM was successfully synthesized after conducting a series of experiments. However, whether the NPAM meets fracturing requirements is unclear. This section presents the performance of gel fracturing fluids based on synthetic NPAMs and a zirconium acetate crosslinker. Generally, polymers with larger molecular weights will increase the gel strength and decrease the gelation time when crosslinking with zirconium acetate. Because of its easy operation and simple construction, the low molecular weight polymer was synthesized as the gel fracturing fluid. In this study, NPAM used as the crosslinked gel fracturing fluid and was synthesized with 16% AM and 0.01% initiator concentrations at a feeding temperature of 52° C and a reaction temperature of 62° C for 4 h; the resultant molecular weight was 6,648,600 g/mol. Accordingly, the gelation time, shear resistance, filtration performance, gel breaking



Figure 7. The contour map of gelation time of gel fracturing fluid.



Figure 8. The shear resistance capacity of gel fracturing fluid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

performance, proppant carrying capability, and core damage capability were investigated.

Gelation Time. To make fractures and to carry proppant, it is necessary for NPAM and zirconium acetate crosslinker to quickly form high viscosity gel fracturing fluids in a very short time. The NPAM concentration was varied from 0.2 to 0.4% whereas the crosslinker concentration was varied from 1.5 to 2.5%. Figure 7 shows that the gel fracturing fluids with higher polymer or crosslinker concentrations can be formed more rapidly than the gels with lower polymer or crosslinker concentrations. However, the gelation time can be reduced to 7.9 min by varying the NPAM or crosslinker concentrations and thus ensuring fluid injection into the formation.

Shear Resistance. As fluids are injected into a formation, the viscosity will decrease due to shear degradation. However, when the viscosity decreases to less than 50 mPa·s, the gel fluids have insufficient strength to carry proppants into the formation and thus cannot form cracks, resulting in a failed fracturing treatment. In this research, the gel fluid shear resistance was deter-



Figure 9. Static filtration curves at three different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]



Figure 10. Static filtration coefficient at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mined using a Haake Rheostree RS75 rheometer with a concentric cylinder system at a shear rate of 170 s^{-1} . Figure 8 shows viscosity changes in the entire shear process at 60, 90, and 120° C. The results show that the gel fracturing fluid viscosity decreases while shear time increases, but remains above 50 mPa·s after shearing for 120 min, which correlates with general technical conditions for the fracturing fluid. This is because the carboxylate group (-COO⁻) on polymer chains can be cross-linked with Zr(IV) ligands in solution, causing the obtained gel fracturing fluid to have a strong mechanical response, resulting in no further decreases in the viscosity.

Static Filtration Performance. Fluid filtration on the formation rock surface typically results in filtrate invasion from fracturing fluids into the reservoir which directly affects the fracturing performance. The large fracturing fluid loss yields a small fracturing volume, reduces the fracture length and width, and results in a failed treatment. Therefore, a good fracturing fluid must have low filtration properties. Generally, the filtration coefficient is used to evaluate the filtration performance of the fracturing fluid. In this study, the gel fracturing formulations, 0.30% NPAM+1.5% crosslinker, 0.35% NPAM +2.0% crosslinker, and 0.40% NPAM +2.0% crosslinker, were, respectively, used at 60, 90, and 120°C. Figure 9 shows that the static filtration curves of the gel fracturing fluid at three different temperatures are straight lines. The static filtration coefficient can be calculated by these three lines (Figure 10). The results show that three static filtration coefficients are lower than the industry standard value of 0.001 m/min^{1/2} at 30°C, which is conducive to forming larger cracks when gel fracturing fluids are injected into the formation. Therefore, the synthetic NPAM used for gel fracturing fluids satisfies filtration performance requirements for fracturing treatments.

Proppant-Carrying Performance. Settlement occurs when the gel fracturing fluid flows through the injection equipment and formation. If the settling velocity is too high, the proppant will quickly settle in the gel fracturing fluid preventing the proppant from entering all cracks. As a result, the proppant will likely plug the wellbore or cracks, leading to a failed fracturing treatment. Therefore, the gel fracturing fluid must have a good

Table IV. Proppant Settling Velocities of Gel Fracturing Fluid

Formula	Temperature (°C)	Settling velocity (10 ⁻³ mm/s)
0.30% NPAM+1.5% Crosslinker	60	0.8
0.35% NPAM +2.0% Crosslinker	90	1.1
0.40% NPAM +2.0% Crosslinker	120	1.2

proppant-carrying capacity. Table IV shows the proppant settling velocities of gel fracturing fluids. The results show that three formulae of gel fracturing fluids have low settling velocities; additionally, the results show that the settling velocity increases slightly at high temperatures. However, the gel fracturing fluid can still satisfy the proppant-carrying requirements for fracturing treatments.

Gel Breaking Performance. The gel fracturing fluid must flow back when cracks are formed. Otherwise, unbroken gel can result in formation damage and a reduction in productivity, rendering the whole fracturing process ineffective. Therefore, the gel fracturing fluid should ideally quickly break and completely flow back after construction. Generally, APS is used as a gel breaking agent.²⁹ In the preparation of the gel fracturing fluid, APS is directly added into the fluid. Then, the fluid is heated in an oven and frequently inspected to monitor the fluid viscosity. According to the SY/T 6376-2008 standard, the time at which the viscosity decreases below 5 mPa·s is the gel breaking time. Figure 11 shows that three types of gel fracturing fluid can be effectively broken within 270 min. Gel fluids with higher APS concentrations can break more rapidly at high temperatures. APS is a very strong oxidizer that forms free oxygen radicals at high temperatures; thus, these free radicals attack the backbone of the polymer strand and break it down, leading to a decrease



Figure 11. Gel breaking performance at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 12. Core damage caused by gel fracturing fluid at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the fluid viscosity. An increase in the APS concentration results in more free radicals, which accelerates the oxidation reactions. Additionally, as the temperature increases, oxidizers become more and more reactive and the reaction rate between the free radicals and the polymer also increases. As a result, the fluid viscosity decreases with increasing APS concentration and temperature.

Core Damage Caused by Gel Fracturing Fluid. Core damage is an important factor used to evaluate a fracturing fluid. An unbroken gel can cause severe reductions in the proppant pack permeability and thus affects fracture conductivity. In addition, gel fracture fluids leaking into a formation can also cause damage to the fracture face, which decreases the formation permeability outside the fracture and affects the fracturing effect. Therefore, a good gel fracturing fluid must have low core damage factors. Tests were conducted with three cores with the same permeability of $0.35 \ \mu\text{m}^2$ at 60, 90, and 120°C . All experimental procedures were conducted according to the SY-T5107-200 standard. Figure 12 shows that three different fracturing fluids can result in core damage, but the damage rates were less than 20%, which satisfies construction site requirements.

CONCLUSIONS

In this work, controlled molecular weight NPAMs were successfully synthesized by an aqueous solution polymerization method. The effect of the monomer concentration, initiator concentration, reaction time, feeding temperature and reaction temperature on the molecular weight were investigated. Controlled molecular weight NPAMs can be synthesized by adjusting these factors. The decisive factor is the monomer concentration, which is the building block during polymerization, whereas the initiator concentration and feeding temperature are secondary factors. A synthetic NPAM can be crosslinked with zirconium acetate to produce a gel fracturing fluid for use in low permeability oil reservoirs. The viscosity remains greater than 50 mPa·s after shearing for 120 min at 120°C, and the static filtration coefficients are lower than 0.001 m/min^{1/2} at 30°C. Gel breaking becomes easier as the temperature increases. The proppant-carrying capacity of the gel fracturing fluid is excellent, and the settling velocity is lower than 1.2×10^{-3} mm/s, whereas the core damage rates are less than 20%. These performances ensure successful gel fracturing and may provide a reference for the development of gel fracturing technology worldwide.

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