INTRODUCTION

With increasing demands on the gas and oil, the demands for exploitation of shale oil and gas increase. Shale is composed of rich sedimentary rocks, which are water-sensitive according to their composition, cracks and fractures, crystalline structure, and porosity.¹⁻³ When contacting with water-based fluid, shale can adsorb water and swell, which generate several problems for drilling, such as caving, bit balling, drag tight hole, and so on.⁴⁻⁶ In order to overcome these problems, oil-based drilling fluids are the preferred drilling fluids, because it has benefits of well inhibition ability, temperature resistance, and lubricity. But it has some inevitable shortcomings, like environmental

Synthesis and mechanism research of a new low molecular weight shale inhibitor on swelling of sodium montmorillonite

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Abstract
Shale gas as green and clean energy is attracting more interest. However, shale hydration and swelling have become the major challenges using water-based drilling fluids, replacing oil-based drilling fluids, for developing shale gas. In this work, a low molecular weight branched polyamine (NETS) as clay swelling inhibitor was synthesized. The NETS performed excellent inhibition property by linear expansion experiments and cuttings hot-rolling recovery. The inhibition mechanism of NETS was investigated using X-ray diffraction, fourier transform infrared spectroscopy, cation exchange capacity, X-ray photoelectron spectroscopy, scanning electron microscopy, and zeta potential. The results show that the NETS can adsorb on Na-Mt, decrease the basal spacing of wet Na-Mt from 1.91 to 1.43 nm, and replace majority sodium ions from interlayer of Na-Mt. However, replaceability of sodium ions and inhibition of water molecules of ethylenediamine are worse than NETS. These indicate that the primary amines of NETS had strong interaction with Na-Mt, tensed clay layers and decrease the basal spacing. The combination of long hydrophobic chain and primary amines makes NETS to adsorb on surface of Na-Mt, intercalate into interlayer of Na-Mt with tilted monolayer arrangement, and replace sodium ions. The more the number of primary amine groups, the better the inhibition performance. Therefore, NETS has a great potential to be an outstanding shale inhibitor of water-based drilling fluids in the future.

KEYWORDS
intercalation mechanism, shale inhibitor, sodium montmorillonite, synthesis

1 | INTRODUCTION

With increasing demands on the gas and oil, the demands for exploitation of shale oil and gas increase. Shale is composed of rich sedimentary rocks, which are water-sensitive according to their composition, cracks and fractures, crystalline structure, and porosity.¹⁻³ When contacting with water-based fluid, shale can adsorb water and swell, which generate several problems for drilling, such as caving, bit balling, drag tight hole, and so on.⁴⁻⁶ In order to overcome these problems, oil-based drilling fluids are the preferred drilling fluids, because it has benefits of well inhibition ability, temperature resistance, and lubricity. But it has some inevitable shortcomings, like environmental
pollution and high cost. Therefore, developing a kind of water-based drilling fluids, which has similar performance with oil-based drilling fluids, has been the main goal for many researchers.7

For water-based drilling fluids, the critical thing is diminishing its impact on shale stability. Many chemicals, as inorganic salts, silicates, and polyglycols, have been developed to relieve or solve the problem of shale stability.7-10 Among these chemicals, potassium was first used to inhibit shale hydration. Then, brines, ammonium, and amine-based chemistry had developed for shale inhibitors of water-based drilling fluids.11,12 Since 1960s, a large numbers of amine compounds have been used in the field.13-15 Recent researches focused on polymer molecular inhibitors. Polyether amine, amine-terminated hyperbranched, and polyethyleneimine had been proven as effective inhibitors.16,17 These large polymer molecules as inhibitors can intercalate into Na-Mt and expand the interlayer space. The expansion of interlayer space is harmful to the inhibition ability. What is more, some researchers have realized that the smaller molecular weight causes lower expenses, better water-solubility, and some special properties.18-20 However, the small inhibitor molecules with low number of groups exhibit limited inhibition. Therefore, this paper focuses on the synthesis of branched polyamine with low molecular weight as clay swelling inhibitor and its intercalation inhibiting mechanism.

In this paper, a kind of novel low molecular weight inhibitor was synthesized. The inhibition performance of inhibitor was investigated by linear expansion experiments, cuttings hot-rolling recovery. Its inhibition mechanism was explored by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), cation exchange capacity (CEC), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and zeta potential. This synthesized inhibitor exhibited excellent inhibition performance and had a great potential to be an outstanding shale inhibitor of water-based drilling fluids in the future.

2 | EXPERIMENTAL

2.1 | Materials

The chemical composition of Na-Mt (obtained from the Nanocor Company) is 71.30% SiO₂, 13.22% Al₂O₃, 4.79% Na₂O, 7.10% MgO, and 3.59% Fe₂O₃. The cation exchange capacity (CEC) of Na-Mt is 113 meq/100 g. Ethylenediamine (EDTB), HBr, AcOH, EtOH, KCl, and NaCl were purchased from Cheng Du Micxy Chemical Co., Ltd. N-(Phenylsulfonyl) aziridine (NTS) was purchased from Hangzhou Yajian Biotech Co., Ltd.

2.2 | Synthesis and characterization

Tosylaziridine is useful material that allows the primary amine group to be attached to an aminoethyl group.21 NTS is a common tosylaziridine. In this paper, NETS was synthesized from reaction of EDTB and NTS, followed by detosylation with HBr/AcOH.

Ethylenediamine (1 mmol) was dissolved in 50 mL absolute ethanol. NTS (4 mmol) was dissolved in 20 mL absolute ethanol. NTS solution was added dropwise to ethylenediamine solution and kept stirred at 25°C for 12 hours. Absolute ethanol was removed by evaporation on a rotavapor at 50°C. A total of 100 mL 30% HBr/AcOH solution was added and the mixture was refluxed for 24 hours at 90°C. The brown-yellow liquid is obtained. The liquid was cooled to room temperature and then placed in an ice bath. The precipitate was filtered and washed with EtOH (25.0 mL × 2) to get the final product, brown-yellow solid. The N1,N1'-(ethane-1,2-diyl)bis(N1-(2-aminoethyl)ethane-1,2-diamine) (NETS) synthesis reactions are presented in Figure 1. Yield: 75%. IR (KBr, cm⁻¹): 3442, 2954, 2865, 1600, 1217, 1450, as shown in the Figure S1; ESI-MS calcd for C₁₀H₂₈N₆ (M⁺): 233.24, found 233.25, as shown in the Figure S2.

2.3 | Sample preparation

Na-Mt was dried at 150°C for 24 hours. Na-Mt dispersion was formed from 1 g Na-Mt stirred 3 hours at 30°C with 25 mL distilled water. Then, the dispersion was added 25 mL NETS or EDTB solution with different concentrations at 30°C. The dispersion was stirred for 24 hours and then centrifuged at a speed of 5550 g for 25 minutes. The centrifugal sediment was added 25 mL distilled water, and the mixture was stirred with glassrod at room temperature. Centrifuged and washed three times as above. Wet Na-Mt/NETS or wet Na-Mt/EDTB sample was prepared by above processes. Dry Na-Mt/NETS or dry Na-Mt/EDTB sample can be gained by drying wet sample at 150°C for 24 hours and fully blending.

2.4 | Linear expansion experiment

A total of 10 ± 0.01 g drilling cuttings were passed through 100 mesh sieve and dried in 105°C ± 3°C for 4 hours. The drilling cuttings were put in the test tube and smoothed. Using pressing machine, drilling cuttings were compressed by 4 MPa for 5 minutes. The pressure was removed. The depth of cylinder (H) was measured with Vernier caliper.
After the linear dilatometer was preheated for 30 minutes, the test tube with drilling cuttings was installed in the instrument. The 1% inhibitor solution was filled into the test tube. At the same time, the stopwatch was started and recorded the display values of 2 and 16 hours. The linear expansion ratio was calculated by the below Equation 1.

\[ W = \frac{(R_t - R_1)}{H} \times 100\% \]  

where \( W \) is the linear expansion ratio, \%; \( H \) is the original depth (\( H \)) of the drill cuttings, mm; \( R_1 \) is the initial reading, mm; \( R_2 \) is the 2 hours reading, mm; \( R_{16} \) is the 16 hours reading, mm.

### 2.5 Hot-rolling test

A total of 50 ± 0.01 g drill cuttings were passed through 100 mesh sieve and dried in 105°C ± 3°C for 4 hours. The drilling cuttings were put into high-temperature aging tanks with 350 mL 1% inhibitor solution. The tanks were put into the heating furnace at 80°C for 16 hours. After high-temperature aging, the drill cuttings were passed through 40-mesh sieves with water and then dried in 105°C ± 3°C for 4 hours. Cuttings were cooled to room temperature and weighed (\( M \)). The first-roller recovery (\( R_1 \)) of the drill cuttings was calculated by Equation 2. The 350 mL new configured solutions were added high-temperature aging tanks with drill cuttings. After repeating the above steps, the second and third roller recovery of drill cuttings (\( R_2, R_3 \)) was calculated.

\[ R = \frac{M}{50} \times 100\% \]  

where, \( M \) is the recycling quantity; \( R \) is the roller recovery of drill cuttings, %.

### 2.6 Inhibition mechanism analysis

Two mg dry Na-Mt/NETS or dry Na-Mt/EDTB powder and 20 mg KBr were mixed fully and compressed. FTIR of the compacted tableting was obtained on a Nicolet 6700 FTIR spectrometer (Thermo Scientific Corporation).

The wet and dry Na-Mt/NETS or dry Na-Mt/EDTB samples were poured into the groove of glass slide. The XRD pattern of samples were obtained by X'Pert PRO MPD diffractometer (a Cu Kα radiation source), and 2θ angle was scanned between 3° and 40°. The basal spacing of samples was analyzed by Bragg's equation (\( 2d \sin \theta = n \lambda \), \( \lambda = 1.5406 \) nm, \( n = 1 \)).

Dry Na-Mt/NETS or dry Na-Mt/EDTB sample was sieved through 2 mm sieve hole. Five g dry sample was used to test. Test method was Ammonium chloride-ammonium acetate process.

Wet Na-Mt/NETS or wet Na-Mt/EDTB samples were adhered on the sample holder and were freeze by liquid nitrogen. The samples were metal sprayed for 2 minutes. SEM analysis was performed by a Quanta 650F scanning electron microscope.

Two gram dry Na-Mt/NETS or dry Na-Mt/EDTB powder be loaded into the mold and compacted with 50 MPa pressure. The compacted samples were dried at 100°C for 24 hours. Spectra sans of C, N, O, Si, Mg, and Al were carried out. The XPS analysis of compacted samples was tested by ESCALAB 250X-ray photoelectron spectrometer.

Different amounts of inhibitors of wet Na-Mt/NETS or wet Na-Mt/EDTB samples were prepared and dispersed by ultrasonicator for 30 minutes. The dispersions were test by ZetaProbe (Colloidal Dynamics).

METTLER TGA/DSC1 instrument was used to measure the adsorbed water of Na-Mt. The heating rate is 15°C/min from 30 to 300°C. The rate of nitrogen flow was 60 mL/min.
3 | RESULTS AND DISCUSSION

3.1 | Linear expansion experiment

The type of drilling fluids directly affects the levels of shale swelling.22 Though linear swelling test still has drawbacks, it can be regarded as a widely recognized evaluation method of shale expansibility.23 In this paper, linear swelling rate was used to evaluate the inhibition of the synthesized NETS against the swelling of bentonite.

The linear expansivity values with different inhibitor system and deionized water were measured and showed in Figure 2. Compared with the value of deionized water, the linear expansivity values in potassium chloride, sodium chloride, NETS, and EDTB system all decreased in 2 and 16 hours. That implied the four inhibitors could inhibit swelling of shale. Specifically, the synthesized inhibitor NETS exhibited better inhibitive ability than EDTB, potassium chloride, and sodium chloride, which were often used as inhibitors in situ.

3.2 | Cuttings hot-rolling recovery test

Cuttings hot-rolling recovery test had been used to evaluate swelling ability of shale, and better inhibitive ability of an inhibitor can be indicated by higher cuttings recovery rate.24

After rolling at 80°C for 16 hours, the cutting recovery rate for different inhibitor systems was measured. And result is shown in Figure 3. Comparing to the rate of deionized water, the other three inhibitor systems were significantly improved. More importantly, the synthesized inhibitor NETS had the highest cutting recovery rate than potassium chloride, sodium chloride, and EDTB, which indicates NETS has better inhibitive ability.

3.3 | Inhibition mechanism analysis

3.3.1 | Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy is a useful way to qualitatively determine the chemical composition of materials and interaction between molecules. As shown in Figure 4, the vibration bands of pristine Na-Mt coincided...
with the published paper well. In the FTIR spectra of Na-Mt/NETS, the typical characteristic bands of original Na-Mt and NETS were presented, which indicated the successful adsorption of NETS onto Na-Mt. The peaks at 2929 and 2840 cm\(^{-1}\) are attributable to C-H stretching vibration of alkyl group. The bands at 3226 cm\(^{-1}\) are attributable to the C-N stretching vibration. Those indicate that both EDTB and NETS had been successful physical adsorption onto Na-Mt.

### 3.3.2 X-ray diffraction

X-ray diffraction was often used to insight state of interlayer of Mt by measuring the basal spacing of Na-Mt. The XRD patterns of Na-Mt/NETS and Na-Mt/EDTB under dry and wet conditions in Figure 5. The basal spacing of pristine dry Na-Mt and wet Na-Mt is 1.01 and 1.91 nm, respectively. After treated with 1% (w/w) of EDTB, the basal spacing of wet Na-Mt decreased from 1.91 to 1.45 nm. When adding amount more than 2% (w/w) of EDTB, the basal spacing of wet Na-Mt decreased to 1.35 nm. The basal spacing of dry Na-Mt/EDTB was still 1.29 nm and did not change.
with different concentration. After modification by 1% (w/w) of NETS, the basal spacing of wet Na-Mt declined significantly from 1.91 to 1.43 nm and without change when increasing NETS concentration, which indicated that NETS could decrease of interlayer water by tensing clay layers.29,30 Compared with wet Na-Mt/NETS and dry Na-Mt/NETS, the basal spacing of Na-Mt decreased from 1.43 to 1.29 nm, indicating that NETS intercalated into clay interlayer with tilted monolayer arrangement. At the minimum inhibitors, the basal spacing of wet Na-Mt/NETS was lower than that of wet Na-Mt/EDTB, indicating that NETS had better inhibition performance than EDTB at low adding amount.

### 3.3.3 Cation exchange capacity

The ammonium method is a reliable approach to measure the cation exchange capacity of inhibitors intercalated in Na-Mt. Ammonium acetate is considered able to replace the exchangeable cations and adsorb on the exchange sites of the Na-Mt surface. Na-Mt was treated with different concentration of inhibitors and measured CEC. The CEC values of Na-Mt, Na-Mt/EDTB, and Na-Mt/NETS were shown in Table 1. After treated with EDTB, CEC values of Na-Mt were almost unchanged. Compared with Na-Mt/EDTB, CEC values of Na-Mt/NETS rapidly decreased from 113.00 mmol/100 g to 28.21 mmol/100 g and did not change with increasing concentration of NETS. The results indicated that NETS can replace sodium ions of Na-Mt, which is the main cause of sodium montmorillonite hydration, and occupy the negatively charged adsorption sites generated by isomorphous replacement. Therefore, replacing hydration cations (sodium ions) is the reason for excellent inhibition performance of NETS. And longer hydrophobic chain could improve inhibition performance of inhibitors.

### 3.3.4 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to evaluate the morphology.32-34 Spherical and sequential layered structures are responsible for good inhibition, and rheological and filtration properties.35 Figure 6 shows SEM images of Na-Mt modified with water, 1 wt% EDTB, and 1 wt% NETS. The SEM images show that the microstructures of the hydrated Na-Mt resembled a crimped leaf. After the addition of 1 wt% of EDTB, the majority of Na-Mt remained curly and scattered, which indicates its weak inhibition potential. These images indicated that NETS can change the morphology of Na-Mt to perfectly spherical structures and a layered structure with more sequential. Therefore, NETS shows excellent inhibition performance and can be a comprehensive performance inhibitor.

### 3.3.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a useful way to investigate the surface composition of Na-Mt, Na-Mt/EDTA, and Na-Mt/NETS. The compositions of these three systems were shown in the XPS surveys (Figure 7). The spectrum of Na-Mt had Na 1s signal, but no N 1s signal, indicating that Na-Mt has sodium ions and no nitrogen ions. Compared with Na-Mt, the N 1s signal of Na-Mt/EDTB increase, which proves EDTB adsorbs on the Na-Mt. The area of Na 1s of Na-Mt/EDTB is almost same with Na-Mt, which indicates that EDTB cannot replace the sodium ions of Na-Mt. This is because thick hydrated film of EDTB blocks the replacement process. The result is verified by the CEC. However, comparing with Na-Mt, the binding energy of Na 1s of Na-Mt/EDTB is lower. EDTB still has potential to replace the sodium ions and decrease the interaction between the sodium ions.

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**FIGURE 7** XPS patterns of dry Na-Mt and Na-Mt/NETS: (a) is Na 1s pattern; (b) is N 1s pattern
ions and clay sheets. The area of Na 1s of Na-Mt/NETS is lower than Na-Mt, but the area of N 1s is higher than Na-Mt. This indicates that NETS can intercalate in the interlayer space of Na-Mt by displacing sodium ions of Na-Mt. The lower interlayer cation content has lower degree of hydration, because the major reason of expansion of montmorillonite is hydration of the interlayer cationic.36,37 NETS could displace most of interlayer cations of Na-Mt and effectively inhibit crystal expansion of Na-Mt.

### 3.3.6 Zeta potential

The electro kinetic properties of Na-Mt were probed by measuring its zeta potential. The Figure 8 shows the zeta potential of Na-Mt with different concentration of inhibitors. The zeta potential of Na-Mt was −33.2 mV and presented well-stable dispersion. The negative surface charge was formed by the isomorphous substitution of clay.38 After adding NETS to Na-Mt, the zeta potential values reduce as many similar results reported.39 The downward trend can be explained by two reasons. First, in water solution amine groups of NETS can be protonated and change into ammonium ions which have positive charge. Ammonium ions could adsorb on the surface of Na-Mt by electrostatic attraction and hydrogen bond interaction, which led to decrease of zeta potential.40 Second, the shielding effect, generated by hydrophobic segment of NETS, would give rise to decrease the thickness of electrical double layer and zeta potential.41,42

### 3.3.7 Thermogravimetric analysis

The thermal properties of Na-Mt, Na-Mt/EDTB, and Na-Mt/NETS were gained by TG and are shown in Figure 9. In these three curves, there is a downward trend at 65°C. And this trend ends at 179°C. This trend is generated by loss of absorbed water of Na-Mt. The more the curve goes down, the more the water absorbed. From the result, the order of degree of decline is Na-Mt (91%) > Na-Mt/EDTB (75%) > Na-Mt/NETS (1%). This indicates that EDTB and NETS have ability of inhibition clay hydration, and NETS has a better ability than EDTB. At 231°C, the TG curve of Na-Mt/NETS has a second falling, which is produced by decomposition of NETS. So the decomposition resistance of NETS was 231°C. Thus, NETS has inhibition effect in the Na-Mt before 231°C.

### 3.3.8 Inhibition mechanism

According to the above experiments, when the low concentrations of NETS were added to the hydrated Na-Mt, the basal spacing of Na-Mt decreased significantly. The basal spacing of Na-Mt maintains unchanged with the increasing of NETS, which indicate that NETS can minimize the basal spacing in a lower concentration. NETS with four primary amine groups enters into the interlayer spacing of Na-Mt, reduces the interlayer spacing of Na-Mt and replaces the sodium ion in the interlayer spacing. Those showed that the interaction of primary amine groups and silicon-oxygen tetrahedra of Na-Mt is greater than that of water molecules caused by van der Waals forces and ionic bonds between adjacent layers of montmorillonite. Therefore, with the primary amine groups, NETS can adsorb on the active site of Na-Mt and replace the counter ions (sodium ions). The chain backbone of NETS with hydrophobic properties can push out the water molecules adsorbed on the interlayer spacing of Na-Mt (Figure 10). The more the number of primary amine groups, the better the inhibition performance. What is
more, when the primary amine groups were protonated, the interaction between protonated primary amine and Na-Mt would be stronger. However, some literatures reported that when the pH value is >7, the protonation degree of primary amine groups is very low.43-45 The results indicated that primary amine groups without protonation also replace the counter ion.

CONCLUSIONS

In this paper, a new low molecule weight shale inhibitor was synthesized and its mechanism was investigated. The results show the NETS showed excellent inhibition performance. It can replace sodium ions of interlayer space and become adsorbed on the interlayer space and surface of Na-Mt. The long alkyl chains of NETS can reduce the thickness of hydration film. Combinations the primary amine and long hydrophobic chain enabled NETS to intercalate in interlayer of Na-Mt with a tilted monolayer arrangement, strain the crystal layer and minimize the basal spacing of Na-Mt from 1.91 to 1.43 nm. Therefore, the water molecules of the clay were expelled. The more the number of primary amine groups, the better the inhibition performance. Overall, NETS had great potential to be an excellent shale inhibitor of water-based drilling fluids to replace oil-based drilling fluids.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section.

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