Preparation and viscoelasticity of a novel hydrophobic associating polymer with salt stimulation responsiveness by functional monomer modification for fracturing fluids

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Abstract

In this study, a salt-resistant hydrophobic association polymer (PZDY) is synthesized by acrylamide, octadecyl dimethylallyl ammonium chloride and decane polyoxyethylene ether acrylate by aqueous polymerization. The infrared spectroscopy, fluorescence spectroscopy, scanning electron microscopy and other characterization methods were used to study its properties, and the rheological properties of PZDY solution is analyzed. The results showed that when concentration of NaCl is less than 5 wt% and CaCl₂ is less than 1 wt%, the viscosity of 0.4 wt% PZDY increases with the increase of salt concentration. When the salt concentration continued to increase, the PZDY viscosity gradually decreased. Investigation of the rheological behavior showed that 0.6 wt% PZDY in 5 wt% NaCl and 1 wt% CaCl₂ solution, could withstand a temperature up to 180 °C, after being sheared for 2500 s at 170 s⁻¹, and its viscosity was greater than 50 mPa·s. Moreover, the viscosity of 0.6 wt% PZDY in 5 wt% NaCl increased from 104 to 205 mPa·s and the viscosity of 0.6 wt% PZDY in 1 wt% CaCl₂ increased from 110 to 157 mPa·s, when at a shear rate of 170 s⁻¹, at 180 °C and the shear time was less than 500 s. Meanwhile, SEM results showed that salt addition enhanced the quasi-spatial network structure, with closer clustering of PZDY molecules in NaCl solution than in CaCl₂ solution. The storage modulus (G') and loss modulus (G'') increased with the increase of PZDY concentration. Therefore, PZDY can be used to improve the heat and shear resistance of fracturing fluids and enhance oil recovery.

1. Introduction

With the gradual decrease of oil storage in high-permeability reservoirs, the development of unconventional oil and gas resources in low-permeability and ultra-low-permeability reservoirs has become an important strategy for the replacement of conventional fossil-fuel energy sources in the petrochemical industry. Especially high temperature, high salinity and low permeability reservoirs, which are expected to cover billions of tons of geological reserves, and have gradually become the main field of tertiary oil production [1]. Polymer flooding plays an important role in enhanced oil recovery (EOR)[2–4]. Polyacrylamide (PAM) plays an irreplaceable role in polymer flooding. However, the amide group in PAM molecules is easy to hydrolyze under acidic and alkaline conditions, and the hydrolysis rate in neutral conditions is also accelerated with the increase in temperature, resulting in polyacrylamide loses the characteristics of temperature and salt resistance. In addition, due to its linear flexible chain segments, its structure is easy to be damaged under high shear conditions. Therefore, PAM is suitable for medium-low temperature and low salt reservoirs. And more stringent requirements have been established for the performance of polymer flooding, such as a low degree of formation damage, high temperature and salt resistance, strong formation adaptability, and environmental friendliness[5–6].

Nowadays, natural plant gum, “clean” surfactants, and synthetic polymers have been widely used as hydraulic fracturing fluids. Although natural plant-gum fracturing fluid has good thickening ability, biodegradability, and biocompatibility, it has poor temperature resistance and greatly damages the reservoir[7–8]. Clean fracturing fluids are low-molecular-weight surfactants that have the advantages of
facile preparation, low friction, low amount of residue, and strong sand-carrying capacity; however, they are expensive and have poor temperature and salt resistance\cite{9-13}. Synthetic-polymer fracturing fluids not only demonstrate good thickening ability, high gel-breaking performance, and high thermal stability, but can also be flexibly designed according to different requirements\cite{14-20}. The research and development of temperature and salt resistance hydrophobically associating polymer additives have become a competitive research topic for oil field and chemical workers in laboratory or field in recent years\cite{21-26}. Hydrophobically associating polymer can form reversible network structure through van der Waals force, hydrogen bond and ionic bond between hydrophobic groups. The viscosity, temperature resistance and salt resistance of the polymer solution can be significantly improved. However, the addition of hydrophobically associated monomers deteriorates the water solubility of polymers. The selection of hydrophobically associated monomers is very important in the synthesis of hydrophobically associated polymers.

In this study, the molecular structure of the polymer was optimized to improve its salt resistance. Hydrophilic acrylamide was used as the molecular skeleton; octadecyl dimethylallyl ammonium chloride (DAC) was used as the cationic hydrophobic monomer; and the self-made, salt-resistant, non-ionic functional monomer isodecyl polyoxyethylene ether acrylate (ZDY) was introduced. A hydrophobically associating polymer (PZDY) with a fast dissolution rate and strong association was prepared via free-radical aqueous solution polymerization. The temperature and salt resistance of PZDY and its self-assembly behavior and mechanism in ionic metal-salt solution were studied.

2. Experimental Section

2.1. Materials

The chemicals used in this study, along with their manufacturers, are as follows: Acrylamide (AM; technical grade), Henan Mingzhixin Chemical Industry Co., Ltd; potassium persulfate (APS, analytical reagent (AR) grade), Wuxi Yatai Chemical Reagent Co., Ltd; ascorbic acid (V\textsubscript{C}, AR grade), Shandong Deyan Chemical Reagent Co., Ltd.; water-soluble azodiisobutyronitrile (V\textsubscript{50}, AR grade), Hubei Deke Chemical Co., Ltd. (Hubei, China); CaCl\textsubscript{2} and NaCl (both AR grade), Tianjin Dingsheng Xin Chemical Co., Ltd.; anhydrous ethanol (AR grade), Zhengzhou Zhuoli Chemical Co., Ltd.; isomeric decol polyoxyethylene ether (AEO-10-9, industrial grade), Jiangsu Province Hai ’an Petrochemical Plant Co., Ltd.; triethylamine (TEA; AR grade), Shanghai Xilong Chemical Co., Ltd.; dichloromethane (DMC, AR grade), Shandong Tianmao Chemical Co., Ltd.; acryloyl chloride (AC, AR grade), Shandong Zibo Ward Chemical Chemical Technology Co., Ltd.; azobisobutyronitrile (AIBN; AR grade), lauryl sodium sulfate (SDS; AR grade), Sinopharm Chemical Reagent Co., Ltd.; and octadecyl dimethyl allyl ammonium chloride (DAC; industrial grade), Shaanxi Changhai Oil Field Additives Co., Ltd.

2.2 Preparation of ZDY
ZDY was prepared by the following procedures. Firstly, after 0.3 mol AEO-10-9, 0.35 mol TEA and 250 mL DMC were sequentially added into a dry 500 mL three-necked flask fitted with a stirrer and thermometer and reacted in an ice-water bath for 0.5 h. The reaction system temperature dropped to below 0 °C. Secondly, after 70 mL DMC containing 0.43 mol AC was poured into a dropping funnel and added dropwise to the three-necked flask. Thirdly, after the reaction was proceeded at 0 ~ 5°C for 14 h, DMC was removed by vacuum distillation, then raw product was washed by anhydrous ethanol and acetone three times, respectively. Finally, the product was dried at 40°C vacuum oven for 24 h, and ZDY was got, (yield 74.5%), the forming process of PZDY is shown in Fig. 1.

2.3 Synthesis of PZDY

PZDY was synthesized by water free-radical copolymerization technique. Firstly, after 5 mol AM, 0.06 mol DAC, 0.05 mol ZDY and 0.03 mol SDS and 33.34 mol deionized water were added into the beaker and stirred for 30 min, the pH value of solution was adjusted within 7-7.5 by 30 wt% NaOH solution. Ice is used to cool down the neutralization process, and the temperature of neutralization solution is always lower than 25 °C. Secondly, to increase the molecular weight of the product, a low-temperature initiation method was adopted, and the temperature of the reaction system was reduced to 7°C. Then, inject N₂ for 0.5 h to ensure the complete removal of trapped air. And then, 0.002 mol APS, 0.001 mol VC, 0.0004 mol V50, and 0.003 mol AIBN were sequentially added into the reactor, the N₂ flow throughout the system was stopped when the solution became sticky, and the reaction kettle was sealed and placed in the thermal insulation sleeve. Temperature changes in the system were recorded every 0.5 h until the temperature rose to 60 ~ 80 °C, and the reaction was considered to be complete. After cooling, the glue was removed, cut into pieces. Subsequently, copolymer was washed and extracted with ethanol to remove water, residual monomers and initiators. Finally, PZDY was further dried under vacuous environment at 50°C for 24 h. The forming process of PZDY is shown in Fig. 1.

2.4 Structural Characterization

Fourier-transform infrared (FT-IR) spectroscopy was performed in the wavenumber range of 400–4000 cm⁻¹ using an FT-IR spectrometer (Vector 22, Bruker, Germany). The samples were prepared using the KBr pellet method. The test samples were dissolved in D₂O and transferred into a specialized nuclear magnetic resonance (NMR) tube to acquire their ¹H-NMR spectra using an Avance III spectrometer (Bruker, Germany). The 0.1wt % polymer PZDY was prepared with deionized water, 5 wt% NaCl and 1 wt% CaCl₂ as solvents, respectively. The PZDY was freeze-dried under 0.1 Pa vacuum for 72 h to completely remove the water. Subsequently, the samples were laid flat on a conductive adhesive, gold-sputtered, and then fixed onto a stage to observe their surface morphologies using a scanning electron microscope (SEM; Q45, FEI, USA) equipped with an energy dispersive X-ray (EDX) system (EDAX; Octane Prime; Ametek, USA) with an accelerating voltage of 15 kV.

2.5 Property Measurement

2.5.1 Fluorescence of PZDY Solution
Fluorescence spectroscopy was performed by a Thermo Fisher Scientific Lumina fluorescence spectrophotometer. As a fluorescent probe, pyrene determines the polarity of the microenvironment around the probe by the ratio of $I_1$ and $I_3$ \cite{27}. Firstly, aqueous PZDY solutions with different concentration were prepared. Then, a $5 \times 10^{-5}$ L pyrene solution or $1 \times 10^{-3}$ mol/L ethanol solution was transferred to a 50 mL volumetric flask. Then, $N_2$ was delivered through the edge of the flask, and the ethanol was dried. The aqueous polymer solution was added to the scale line, sonicated in a water bath for 30 min, purged with $N_2$ for 30 min to remove dissolved $O_2$, and left to stand for 24 h. Finally, the fluorescence spectrum of pyrene in the PZDY solution was measured using a Lumina fluorescence spectrophotometer at 25 ℃ with an excitation wavelength of 335 nm in the scanning range of 350 ~ 450 nm \cite{28}.

2.5.2 Salt Resistance of PZDY Solution

Aqueous solutions containing different concentration of NaCl and CaCl$_2$ and, 0.4 wt% PZDY were prepared. The apparent viscosities of the PZDY solutions were measured at 30 ℃ and 170 s$^{-1}$ using a six-speed viscosimeter (ZNN-D6B; Qingdao Shenyu Petroleum Machinery Co. Ltd. China).

2.5.3 Rheological property test of PZDY solution

Solutions containing 0.1 wt%, 0.3 wt%, and 0.6 wt% PZDY were prepared using deionized water, 1 wt% CaCl$_2$ solution, and 5 wt% NaCl solution as solvents. The rheological properties of the solutions were measured using a rheometer (HAAKE™ MARS™; HAAKE, Germany) with a double-walled cylinder. A shear rate of 170 s$^{-1}$ in the temperature range of 30–90 ℃, 30–120 ℃, and 30–180 ℃ were used to analyze changes in the solution viscosity.

2.5.4 Viscoelastic test of PZDY solution

The aforementioned polymer solutions were subjected to strain sweeps (sweep range: 0.1–100) using the rheometer at a temperature of 30℃ and a frequency of 1 Hz to analyze changes in the storage modulus ($G'$) and loss modulus ($G''$), and to determine the linear viscoelastic region. Subsequently, frequency sweeps were performed at a constant strain (sweep range: 0.1–10 Hz) to observe changes in $G'$ and $G''$.

3. Results And Discussion

3.1 Structural Characterization

The structure of PZDY was characterized using FT-IR spectroscopy, and the results are shown in Fig. 2(a). The absorption peak at 3697 cm$^{-1}$ corresponds to the stretching vibration of the N–H bond in PZDY. The C–H stretching vibrations of –CH$_3$ and –CH$_2$ groups appear at 2903 and 2780 cm$^{-1}$, respectively, and the C–H bending vibration occurs at 1510 cm$^{-1}$. The telescopic vibration of the C O bond occurs at 1739 cm$^{-1}$. Absorption peaks corresponding to the stretching vibrations of the ether C–O–C and amide C–N bonds appear at 1269 cm$^{-1}$. The very weak absorption peak at 741 cm$^{-1}$ is attributed to –(CH$_2$)$_{17}$– in the
hydrophobic chain of polymeric PZDY. Therefore, the spectral assignments are in good agreement with the molecular structure of PZDY.

The $^1$HNMR spectrum of PZDY is shown in Fig. 2(b). The peak at $\delta$ 4.70 is the solvent peak of D$_2$O, $\delta$ 1.06 (a) corresponds to the methyl (–CH$_3$) protons, $\delta$ 1.17 (b) to the methylene protons (–(CH$_2$)$_{17}$–) in DAC, and $\delta$ 1.53 (c) to the methylene protons (–CH$_2$–) in ZDY. The following resonances also occur: $\delta$ 1.60 ~ 1.66 (d) and $\delta$ 2.06 ~ 2.15 (e), –CH$_2$–CH–; $\delta$ 3.22 (g), –CH$_3$ in the quaternary ammonium salt; $\delta$ 3.46 ~ 3.57 (h), CH$_2$CH$_2$O– in ZDY. The multiplets at $\delta$ 1.60 ~ 1.66 (d) and $\delta$ 2.16 ~ 2.28 (f) arise from the –CH$_2$–CH– groups of ZDY. The spectrum of the synthesized hydrophobic association polymer PZDY agrees well with the reference spectrum of PZDY.

### 3.2 Determination of Critical-Association Mass Fraction of PZDY

Figure 3 shows the Effect of PZDY concentration on apparent viscosity. It can be seen from Fig. 3, the apparent viscosity of the PZDY solution slowly increases with the increase in PZDY concentration. When the concentration of PZDY reaches a certain value, the apparent viscosity of the solution rises sharply, and a turning point appears in the concentration–viscosity curve, namely the critical association mass fraction ($W^*$). This point indicates that the intramolecular interactions in the solution are replaced with intermolecular interactions upon addition of the ZDY hydrophobic monomer owing to the self-aggregation behavior of PZDY. When the PZDY mass fraction exceeds 0.32 wt%, the self-aggregation behavior of the PZDY molecules is dominated by intermolecular hydrophobic association, forming a quasi-spatial network structure that increases the hydromechanical volume of the molecular line cluster as well as the apparent viscosity.

The hydrophobically associating polymer spontaneously forms micelles and small hydrophobic microregions, which can dissolve pyrene and act as fluorescent probes to signal the intensity of the hydrophobic associating effect. In the fluorescence spectrum, the ratio of the absorbance at 373 nm ($I_1$) to that at 391 nm ($I_3$) is $I_1/I_3$, depending on the polarity of the surrounding environment. When the polarity of the surrounding microenvironment is stronger, the value of $I_1/I_3$ is higher. On the contrary, once the polymer molecules form an obvious dynamic physical crosslinking network, the value of $I_1/I_3$ will decrease significantly [26, 29]. Figure 4 and Fig. 5 show the fluorescence spectra and $I_1/I_3$ changes of pyrene in PZDY solutions with different concentration, respectively. It can be seen from Fig. 4, the fluorescence intensity of pyrene in the solutions with different concentration of PZDY initially increased and then decreased with the increase in wavelength. As can be seen from Fig. 5, the $I_1/I_3$ value decreased with the increase in concentration of PZDY. The fluorescence intensity of pyrene when the concentration of PZDY is 0.30 wt%, the $I_1/I_3$ value suddenly drops, this indicates that when the concentration of PZDY is greater than 0.30 wt%, polymer molecules form a large number of hydrophobic regions, and the polarity of the microenvironment around the pyrene probe weakens. Therefore, the apparent viscosity and fluorescence spectra showed that the $W^*$ value of PZDY was between 0.30 wt% and 0.35 wt%.
3.3 Determination of salt resistance of PZDY

Figure 6 shows the apparent viscosity of the PZDY solution containing different concentrations of NaCl and CaCl$_2$. It can be seen from Fig. 6, the apparent viscosity of conventional partially hydrolyzed polyacrylamide (HPAM) decreases significantly owing to the increase in NaCl and CaCl$_2$ concentration. This is because the conventional HPAM belongs to anionic polymer. In the salt solution, the electric repulsion of carboxyl ions in the polymer will be inhibited, and the molecular chains will curl, resulting in a decrease in the viscosity of the solution. The introduced hydrophobic ZDY monomer can resist the electrostatic shielding effect of inorganic salts, and the charge action of the salt can solubilize the two hydrophobic monomers and increase the volume of the hydrophobic microzone. Therefore, at a certain salt content, the apparent viscosity of PZDY gradually increases with the increase in NaCl and CaCl$_2$ mass fraction. As the mass fraction of the salt continues to increase, the electrostatic shielding effect of the ions is intensified, leading to the crimping of molecular main-chains and a weakening of the solubilizing effect on the hydrophobic monomers; as a result, the apparent viscosity of the polymers begins to decrease gradually. When concentration of NaCl is less than 5 wt%, the viscosity of the polymer increases gradually under the action of salt ions owing to the strong polarity of NaCl, and with the increase in polymer molecular line volume, the apparent viscosity increases. When the concentration of NaCl is greater than 5 wt%, owing to the increase in Na$^+$ content, the electrostatic shielding effect is enhanced, the hydrodynamic volume decreases, and the viscosity decreases accordingly. Figure 6(b) shows that when the concentration of CaCl$_2$ is less than 1 wt%, the viscosity of the polymer increases gradually under the action of salt ions. When the concentration of CaCl$_2$ is less than 1 wt%, owing to the increase in Ca$^{2+}$ content, the charge density increases, compressing the polymer molecules and resulting in molecular-chain crimp and viscosity reduction.

Owing to the special structure of the ZDY-functionalized polyether and the synergistic effect of the hydrogen bond, hydrophobic association, and electrostatic forces in aqueous solution, PZDY has better salt resistance than HPAM. The introduction of ZDY enhances the interactions between polymer chains and stabilizes the molecular structure, allowing the polymer to maintain a high viscosity in highly concentrated inorganic salt solutions.

3.4 SEM analysis of PZDY solution

As can be seen from Fig. 7, deionized water, PZDY molecular aggregation is relatively relaxed and evenly distributed, forming a quasi-spatial network structure. In salt water, the molecules gather more closely together (to a greater extent in NaCl than CaCl$_2$), and the electrostatic shielding of the salt causes the molecular chain to curl\textsuperscript{[30]}. At the same time, the hydrophobic monomers experience a synergistic effect, the associated micelles are stabilized, and the strength of the intermolecular structure increases, improving the salt resistance of the polymer.

3.5 Viscoelasticity of PZDY
Using Deionized water, aqueous NaCl solution (5 wt%), and CaCl$_2$ solution (1 wt%) as solvents, solutions containing 0.1 wt%, 0.3 wt%, and 0.6 wt% PZDY were prepared, respectively. The dependence of $G'$ and $G''$ on stress and frequency is shown in Fig. 8 and Fig. 9. Figure 8 shows that within the stress scanning-range of $0 \sim 10$ Pa, when the PZDY mass fraction is 0.1 wt%, $G' < G''$. A relatively linear plateau is absent, the polymer is mainly viscous, and polymer molecules are mainly associated intramolecularly. When the PZDY mass fraction is 0.3 wt%, the linear plateau appears at a low shear stress. With an increase in shear stress, this plateau disappears, indicating that the polymer intermolecular association is unstable. High shear will destroy the associated structure, resulting in structural changes. When the PZDY mass fraction is 0.6 wt%, $G' > G''$, the linear plateau is relatively stable, and the strongly associated structure can resist intense shearing action. At this point, the elastic polymer molecules mainly form an intermolecular association, and the presence of the salt stabilizes the linear plateau, preventing the system from yielding under high shear stress. Therefore, a stress value of 0.5 Pa was selected along the linear plateau, and a frequency scanning test was carried out on PZDY. The results are shown in Fig. 9.

As can be seen from Fig. 9, within the scanning frequency range of $0.1 \sim 10$ Hz, both the storage modulus ($G'$) and loss modulus ($G''$) of the polymer increase with the increase in frequency. This is because at low frequencies, the PZDY molecular chains are in a relaxed state, and the intermolecular association is weak; as a result, most of the energy is released through the viscosity flow. As the frequency increases, the intramolecular associations partially dissipate to form intermolecular associations; the intermolecular entanglement points increase, initiating crosslinking and thus enhancing the quasi-spatial network structure of the system and gradually increasing $G'$. Under the same conditions, the salt solution has a larger $G'$ and $G''$ than Deionized water because the charge of the salt stimulates the hydrophobic micelle microregion of PZDY and solubilizes the hydrophobic monomer. In solution, the micelles are more closely aggregated, and the viscoelasticity is higher.

### 3.6 Temperature and Shear Resistance of PZDY

Figure 10 shows the temperature and shear resistance of PZDY at 90, 120, and 180 °C. It can be seen from Fig. 10 that in the heating stage, the shear viscosity gradually decreases with the increase in temperature because the thermal movement of molecules is more intense at higher temperatures, and the hydrophobic association is in a chaotic state. When the temperature and shear rate are stable, the intermolecular association is disrupted and in dynamic equilibrium, and the viscosity of the system is also in a stable state. When the system temperature rose to 90, 120, and 180 °C, the viscosity of the PZDY solution basically remained unchanged after shearing, and the final viscosity was 111, 66, and 53 mPa·s, respectively. On the one hand, this can be attributed to the thermal motion of the polymer molecules, which induces associative crosslinking between the molecules in dynamic equilibrium; as a result, the viscosity of the system decreases compared with the steady state condition. On the other hand, increasing the temperature within a certain range can enhance the hydrophobic association strength and increase the apparent viscosity of the solution. Owing to the introduction of the ZDY hydrophobic monomer, PZDY has excellent temperature and shear resistances.
The effects of the salt solution on the rheological properties of the 0.6 wt% PZDY solution (using 1 wt% CaCl₂ solution and 5 wt% NaCl solution as solvents) were measured at 90, 120, and 180 °C at a shear rate of 170 s⁻¹. The results are shown in Fig. 11.

It can be seen from Fig. 11(a), the viscosity of PZDY in the 5 wt% NaCl and 1 wt% CaCl₂ solution exhibit viscosity retentions of 99 and 85 mPa·s, respectively, at 90°C and at a shear rate of 170 s⁻¹. In addition, when the shear time of PZDY in 5 wt% NaCl solution was less than 500 s, the viscosity increased with the increase in temperature, and the salt exerted a certain thickening effect. When the shear time of PZDY in 1 wt% CaCl₂ solution was less than 500 s, the viscosity did not increase greatly with increasing temperature. This is because the introduction of the monovalent salt ion (Na⁺) not only induces the reverse electrolyte effect in the PZDY solution but also significantly increases the hydromechanical volume of PZDY and the polarity of the solution through ionic interactions with the polyether groups in the surrounding ZDY hydrophobic monomer, thus affecting the self-aggregation behavior of the polymer solution. As can be seen from Fig. 11(b), at 120 °C and at a shear rate of 170 s⁻¹, the final viscosity of PZDY in the 1 wt% CaCl₂ and 5 wt% NaCl solutions remained at 65 mPa·s and 72 mPa·s, respectively. As can be seen from Fig. 11(c), at 180 °C and at a shear rate of 170 s⁻¹, the final viscosity of PZDY in the two salt solutions is still greater than 50 mPa·s. Therefore, the PZDY dissolved in 5 wt% NaCl solution has better salt, temperature, and shear resistances than that dissolved in the 1 wt% CaCl₂ solution. To further investigate the temperature and salt resistances of PZDY, the rheological properties of conventional polyacrylamide (PAM) in a 5 wt% NaCl solution and 1 wt% CaCl₂ solution were measured at 90 °C and at a shear rate of 170 s⁻¹ under the same conditions. The results are shown in Fig. 12.

As can be seen from the figure, the salt-thickening phenomenon did not occur in the early shear stage, and the final viscosity was lower than that of PZDY. In conclusion, compared with PAM, PZDY has better temperature and salt resistances.

### 3.7 Analysis of Salt-Tolerance Mechanism

As can be seen from Fig. 13, when the soluble hydrophobic monomer ZDY is added, the number of hydrophobic groups increases, the association between the hydrophobic chains is enhanced, and the supramolecular structure more easily forms, significantly increasing the hydromechanical volume of PZDY. Secondly, the polyoxyethylene ether group of ZDY complexed with metal salt ions, that is, the lone-pair electrons of the oxygen atoms on the oxygen vinyl group were donated into the empty orbitals of the metal-salt ions. In brine, polymolecular aggregation promotes the dissolution of the polymer through complexation, thus enhancing the resistance of the salt ions, the polarity of the functional groups, and the hydrophobicity of the polyether. In addition, the bridging effect of the long hydrophobic chain on the main polymerization chain can be likened to the support of a bridge pier to a bridge deck, increasing the rigidity of the polymer chain as well as the thermal stability. Owing to the synergistic effect of DAC and ZDY, PZDY exhibits excellent rheological properties and salt resistance.
4. Conclusion

(1) The incorporation of the hydrophobic monomer ZDY overcomes the problem of poor salt resistance of the hydrophobic monomer owing to its functional nonionic polyether structure as well its ability to induce hydrophobic association and static electricity. The polymer PZDY shows high temperature tolerance and salt resistance and enables the system to achieve a higher viscosity in highly concentrated solutions of inorganic salts.

(2) The SEM analysis revealed that the PZDY molecules assumed an irregular quasi-spatial network structure in water but more closely aggregated under saline conditions. Owing to electrostatic shielding and the synergistic effect between the hydrophobic monomers, the associated micelles were solubilized, the strength of the intermolecular structure increased, and the salt resistance of the polymer was improved.

(3) The viscoelastic test results indicated that when the mass fraction of PZDY was 0.1 wt%, $G' < G''$, there was no linear plateau, and the viscosity was mainly non-elastic. At 0.3 wt% PZDY transitioned from being intramolecularly associated to intermolecularly associated. At 0.6 wt% PZDY, $G' > G''$, and a linear plateau appeared; the system was mainly elastic. Both $G'$ and $G''$ are higher in salt solution than in Deionized water. Since the charge of the salt stimulates the hydrophobic micelle microregion of PZDY, the hydrophobic monomer is solubilized, the micelles aggregate more closely, and the viscoelasticity is higher.

(4) The rheological property evaluation showed that the viscosity of PZDY remained stable after shearing at 90, 120 and 180 °C at 170 s$^{-1}$; the final viscosities were 111, 66 and 53 mPa·s, respectively. After shearing at 90, 120 and 180 °C at a rate of 170 s$^{-1}$, the final viscosity of PZDY remained above 50 mPa·s in the 1 wt% CaCl$_2$ and 5 wt% NaCl solutions, demonstrating the excellent temperature and shear resistance of PZDY. Especially in 5 wt% NaCl solution, when the shear time was less than 500 s, the viscosity of PZDY increased with increasing temperature, signifying obvious salt-thickening behavior. Therefore, the polymer has excellent salt resistance and broad application prospects.

Declarations

Ethical approval

This declaration is not applicable. Our research does not need to be in humans or animals as research objects.

Competing interests

The authors declare no competing financial interest.

Authors' contributions
Xiaojuan Lai: Conceptualization, Funding Acquisition, , Writing - Review & Editing; Guiru Liu: Conceptualization, Methodology, Software, Investigation, Formal Analysis, Writing - Original Draft, Writing - Review & Editing; Yong Liu: Visualization, Investigation; Xinpeng Dong: Resources, Supervision; Xiaqing Liu: Resources, Supervision; Yasir Mukhtar: Resources, Supervision; Lei Wang: Investigation, Formal Analysis; Xin Wen: Formal Analysis, Supervision; Lijuan Lu: Resources, Supervision.

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**Availability of date and materials**

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**References**


**Figures**

**Figure 1**

Formation of PZDY
Figure 2

FT-IR spectra of ZDY and PZDY (a); $^1$HNMR spectrum of PZDY (b)

Figure 3

Effect of PZDY concentration on apparent viscosity
Figure 4

Fluorescence spectra of pyrene in PZDY solutions with different concentration
Figure 5

Ratio of $I_1/I_3$ of PZDY solutions with different concentration

Figure 6
Effects of different concentration of NaCl (a) and CaCl$_2$ (b) on apparent viscosity of PZDY solutions.

**Figure 7**

SEM images of PDZY in different solvents. (a) 0.1 wt% PZDY in deionized water, (b) 0.1 wt% PZDY in 5 wt% NaCl, and (c) 0.1 wt% PZDY in 1 wt% CaCl$_2$.
Figure 8

$G'$ and $G''$ varying with stress and frequency. (a) PZDY measured in deionized water, (b) PZDY measured in 5 wt% NaCl and (c) PZDY measured in 1 wt% CaCl$_2$. 
Figure 9

Effect of scanning frequency on viscoelasticity of PZDY. (a) PZDY measured in deionized water, (b) PZDY measured in 5 wt% NaCl and (c) PZDY measured in 1 wt% CaCl₂
Figure 10

Plots of thermos-shear measurements of 0.6 wt% PZDY solution. a: at 170 s⁻¹ and 90 °C; b: at 170 s⁻¹ and 120 °C; and c: at 170 s⁻¹ and 180 °C.
Figure 11

Plots of thermos-shear measurements of 0.6 wt% PZDY in salt solutions: (a) at 170 s\(^{-1}\) and 90 °C, (b) at 170 s\(^{-1}\) and 120 °C, and (c) at 170 s\(^{-1}\) and 180 °C
Figure 12

Relationship between apparent viscosity of 0.6 wt% PAM in different solvents were measured at 90 °C and at a shear rate of 170 s⁻¹.
Figure 13

Diagram of salt resistance mechanism of PZDY