



Review Paper

A review of nuclear magnetic resonance (NMR) technology applied in the characterization of polymer gels for petroleum reservoir conformance control



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ABSTRACT

Polymer gel systems have been widely applied to control excessive water and improve oil recovery (IOR) in petroleum reservoirs. They are usually divided into two main types, in-situ cross-linked polymer gels, and pre-formed polymer gels. In recent years, nuclear magnetic resonance (NMR) technology has been gradually applied to the research of polymer gel systems due to its unique analysis advantages. This paper is intent to review these works systematically. For in-situ cross-linked polymer gel systems, NMR can be used to characterize the chemical structure changes of the polymer, the cross-linker, and the auxiliary agent in the formulation of the polymer gel systems. Moreover, the gelation time and the gel strength of the in-situ cross-linked polymer gel systems can also be measured by NMR. For pre-formed polymer gels, NMR can be employed to detect the chemical structure of the designed products. Last, the NMR method can evaluate the plugging, water control, and oil improvement performance of the polymer gels in porous media without using dopants. This review can help readers build a more systematic understanding of the application of NMR technology in polymer gel systems for IOR and help researchers to more deeply study the performance of polymer gel systems.

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1. Introduction

With the development of global mature oil fields, the water cut in production wells has been over 75% mainly due to the petroleum reservoir heterogeneity and the mobility differences between the displacing fluids and the displaced fluids (Seright and Brattekas, 2021; Sydansk, 2011; Zhu et al., 2017a). The excessive produced water not only decreases the oil production but also increases the wastewater treatment cost (Aldaheri et al., 2021; Zhu et al., 2017c). Polymer gel system is one of the most widely used methods to control excessive water production and improve oil recovery (Liang et al., 1992; Seright and Martin, 1991; Zhu et al., 2021a). It can be divided into two main types: in-situ cross-linked polymer gel systems and pre-formed gels (Seright and Brattekas, 2021; Zhu et al., 2017a). For in-situ cross-linked polymer gel systems, the gelant formulated by the polymer, the cross-

linker, and other auxiliary agents is injected into the formation before being cross-linked. Then the injected liquid forms a semi-solid substance with three-dimensional (3D) network structures in high-permeability channels/fractures with designed gelation times (Jia et al., 2020a; Sun et al., 2020; Sydansk and Seright, 2007). Therefore, these water channels will be blocked, and chase fluids will be diverted into un-swept layers with high oil saturation and thus decrease water cut and improve oil recovery (Seright and Brattekas, 2021; Seright, 2009; Sun et al., 2020). The second type of polymer gel system is the pre-formed polymer gel, such as the pre-formed particle gel (PPG) and the polymeric microsphere. They use monomeric polymers such as AM in a ground reaction device to obtain water absorbent particles of different shapes (such as spherical or granular) (Bai et al., 2004; Zhu et al., 2018). Then they are injected into the formation in a form of suspension. These particles continue to absorb water and swell in the formation. After a certain period, high permeability channels will be blocked by these swollen gels, and the chase liquid will be diverted to the un-swept area, thereby improving oil recovery (IOR) (Ding et al., 2020; Imqam et al., 2007).

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Therefore, the evaluation methods of these two polymer gel systems differ from each other because of their different preparation methods and application mechanisms. For the in-situ cross-linked polymer gel systems, the primary evaluation parameters are gelation time, gel strength, long-term stability and the plugging performance in porous media (Yang et al., 2021a; Zhu et al., 2017b, 2017c). Suitable gelation time can guarantee the successful injection of in-situ cross-linked polymer gel systems (e.g., if the gelation time is predicted to be too short, the gel system will block the wellbore). In addition, the appropriate gel strength ensures that the gel system has a specific plugging capacity and abrasion resistance in the formation (Aldhaheeri et al., 2020; Sydansk and Seright, 2007). Common methods for evaluating gelation time and gel strength are Sydansk bottle test (gel code method) (Sydansk and Argabright, 1987), viscosity method (Ji et al., 2000) and rheological test (Al-Muntasheri and Nasr-El-Din, 2007; El-Karsani et al., 2015; Jia et al., 2020b). Sydansk bottle test method can monitor the gelation state for a long time; however, there are significant errors in the results obtained due to the manual reading (Al-Muntasheri and Nasr-El-Din, 2007; Zhu et al., 2019). Viscosity method and rheological test are capable of quantitatively measuring the change in gel strength and thus determining the gelation time, but the gel is continuously sheared during the measurement and cannot be tested for a long time (such as weeks or months) as well (Al-Muntasheri, 2008; Romero-Zeron et al., 2008; Zhang et al., 2021). Moreover, these two methods cannot simulate the gelation performance of the in-situ cross-linked polymer gels in the formation. For pre-formed polymer gels, the gel performance evaluation method is relatively simple, that is, the swelling performance and strength of the gel in different environments (Imqam et al., 2007; Zhu et al., 2018, 2021b). The pre-formed polymer gels can be characterized by conventional methods such as the laser particle size analyzer to measure particle size (Wang et al., 2018a), rheometer or displacement device to measure gel strength (Almahfood and Bai, 2021; Yang et al., 2017), etc. It can be seen from the literature that the critical issue in improving the applicability of the pre-formed polymer gel system for petroleum reservoirs is the introduction of new functional monomers into the polymer gel structure. Therefore, it is critical to characterize the structure of the pre-formed gel system (i.e., to determine whether the functional monomer is successfully introduced into the polymer gel structure).

Based on the problems encountered in the conventional characterization methods (i.e., Sydansk bottle test, viscosity method, and rheological test) of polymer gel systems, researchers and petroleum engineers have gradually introduced nuclear magnetic resonance (NMR) technology into the field of improving oil recovery (Alshehri et al., 2017; Kwak et al., 2017; Liang et al., 2018; Shi et al., 2020). It includes conventional reservoir IOR analysis, unconventional reservoir IOR analysis and polymer gel technology for profile control and water shut-off, and so on (Dong et al., 2020; Du et al., 2020a; Kirkland et al., 2015; Liang et al., 2007; Markovic et al., 2020). The object of this paper is to review the application of NMR technology in polymer gel systems for improving oil recovery. Compared to conventional characterization methods of polymer gels, NMR technology is a non-destructive testing technique that allows for long-term measurements (Al-Muntasheri, 2008; Romero-Zeron et al., 2008; Wang et al., 2021). In addition, since the polymer gel system is mainly composed of carbon and hydrogen atoms, ^{13}C and ^1H NMR methods are often used to evaluate the chemical structure and gelation performance of the gel system (Vargas-Vasquez et al., 2007a). Also, reservoir fluids (e.g., crude oil, natural gas, and water) also contain a large number of hydrogen atoms, and the pore size of the porous medium also has a significant influence on the relaxation time of the hydrogen atom

(Markovic et al., 2020; Shi et al., 2020). Therefore, the gelation, propagation, and plugging performance of the polymer gel system in the porous medium can be monitored by the ^1H NMR technique (Al-Muntasheri, 2008; Kwak et al., 2017). However, the above research is currently in its infancy, and there are not many reports on this aspect, which are also scattered and do not form a specific research logic framework. Moreover, the related review is even less reported.

In this paper, we will review the NMR technology in the performance evaluation and application of polymer gel system for the first time. First, the basic principles of NMR technology and its main types in petroleum engineering, namely conventional NMR method, low field NMR method and nuclear magnetic resonance imaging (MRI) method, will be introduced. Then, the application of NMR technology in chemical structure characterization of polymers and cross-linkers in the formulation of the in-situ cross-linked polymer gel systems and pre-formed polymer gel systems will be reviewed. Next, experimental studies on the evaluation of gelation properties (such as gelation time, gel strength and long-term stability) of the in-situ cross-linked polymer gel system by NMR technology will be carried out. Finally, the application of NMR technology in the evaluation of the plugging performance and gel stability of polymer gel system in porous media will be introduced. Finally, the future works of NMR technology in polymer gel systems are proposed. It can provide new ideas and methods for further development of polymer gel systems, evaluating their gelation performance and plugging performance, and monitoring their performance of conformance control and oil recovery improvement in oil fields.

2. Overview of NMR technology

2.1. NMR fundamentals

NMR technology utilizes the paramagnetism of the nucleus and the applied magnetic field they interact (Liao et al., 2021). A nucleus is a charged system that has spins, so its rotation can produce a magnetic field and a set of vector parameters can represent the strength and direction, that is the nuclear magnetic distance. In the absence of any external field, the nuclear magnetic moment is arranged randomly and irregularly. Under the influence of a fixed uniform strong magnetic field B_0 , the spin system is polarized and the nuclear magnetic distance rearranges and aligns along the direction of the magnetic field. The direction of this field moves at the frequency ω_0 . ω_0 is proportional to the magnetic field strength B_0 , and ω_0 is called the Larmor frequency. In a polarized magnetic field, if an alternating magnetic field B_1 is added in a direction perpendicular to B_0 , and its frequency is the precession frequency of protons (hydrogen nuclei), resonance adsorption occurs, as shown in Fig. 1. The nuclear magnetic moment in a low energy state transitions to a high energy state by absorbing the energy supplied by the alternating magnetic field (Yang et al., 2021b). This phenomenon is called NMR. When the electromagnetic wave is detected to be absorbed, the T_2 absorption spectrum can be obtained, as shown in Fig. 1.

Relaxation contains two ways, T_1 and T_2 relaxation. T_2 is the transverse relaxation time, caused by the exchange of energy within the spin system, also known as the spin-spin relaxation time. The T_2 decay curve includes most of the physical information of the porous medium, and therefore it is the main target of NMR detection. The vertical coordinate in Fig. 1 is the NMR magnetic field intensity, which can be converted to obtain the hydrogen core content in the core (for example, it can sometimes be used to calculate the water saturation in the core). The horizontal coordinate is the NMR transverse relaxation time T_2 , which is

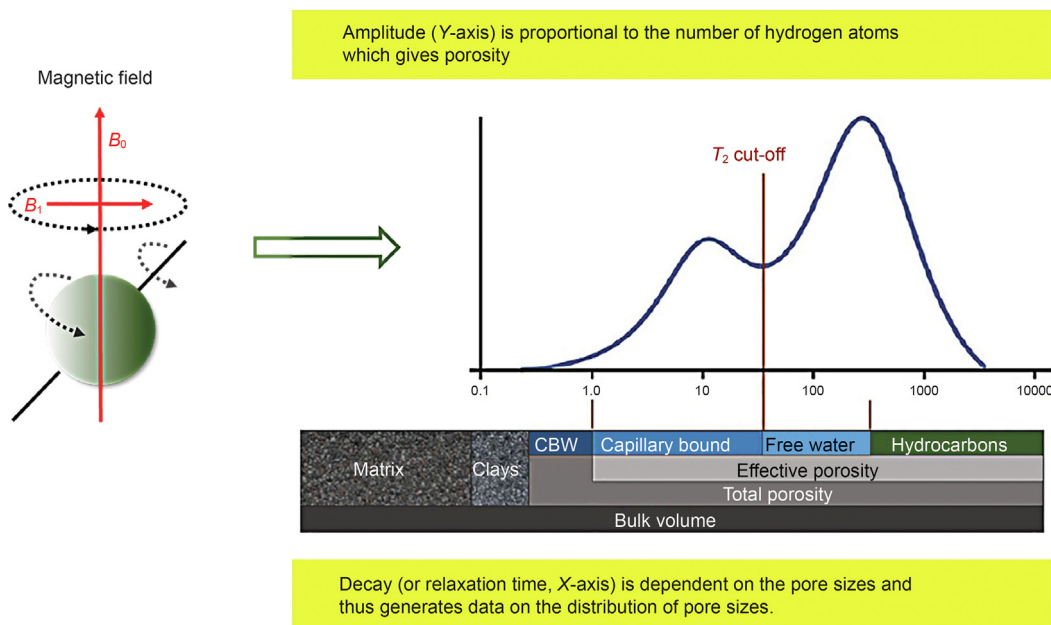


Fig. 1. NMR measurement mechanism (Adapted from McPhee et al., 2015).

proportional to the pore size, and the magnitude of the signal amplitude is proportional to the amount of fluid in the corresponding pore.

2.2. Overview of NMR technology in polymer gels for controlling conformance and improving oil recovery

NMR methods applied in polymer gel systems for controlling conformance and improving oil recovery can be divided into three main types, including conventional NMR method, low field NMR method, and magnetic resonance imaging (MRI) method (Edwards, 2007), as shown in Fig. 2.

For conventional NMR method, it includes the ^{13}C and ^1H NMR method, which can be used to analyze the chemical structures of the polymer and the cross-linker in the formulations of the in-situ cross-linked polymer gels, and also the chemical structures of the pre-formed polymer gels. In addition, it also contains the ^{27}Al NMR method that can be used to analyze the concentration changes of aluminum (Al) during the process of cross-linking between HPAM and Al^{3+} . The low field NMR is widely applied to study the gelation

mechanism between HPAM and chromium acetate (CrAc_3) in recent years, for example, they can characterize the gelation time, gel strength, and gel syneresis of the in-situ cross-linked polymer gels. Moreover, the low field NMR can also be employed to study the influence of media (i.e., in bulk solution or porous media) on the NMR characterization performance. Last, MRI technology can be applied to study the gelation mechanism (for example, the gelation time) as it can monitor the signal intensity changes as the cross-linking proceeds and the gelation performance in porous media by analyzing the fluid saturations in each displacing period. Details will be shown in the following sections.

3. Polymer gel system characterization

Polymer gel systems can be mainly divided into the in-situ cross-linking polymer gels and the preformed gels (Zhu et al., 2017a), as shown in Fig. 3. In-situ cross-linking polymer gels are pumped into the target layer in the form of a solution and formulated by polymers, inorganic and organic cross-linkers, and other auxiliary agents (i.e., oxygen scavengers and reinforcement

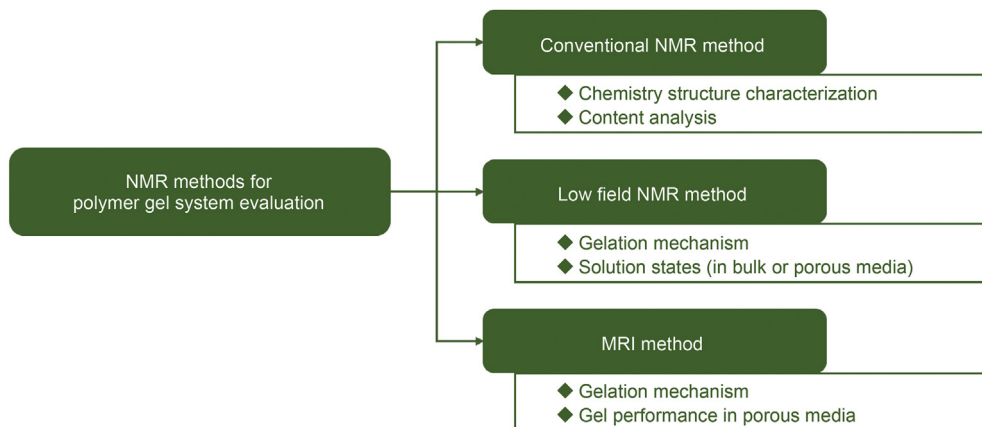


Fig. 2. NMR methods in polymer gel systems evaluation.

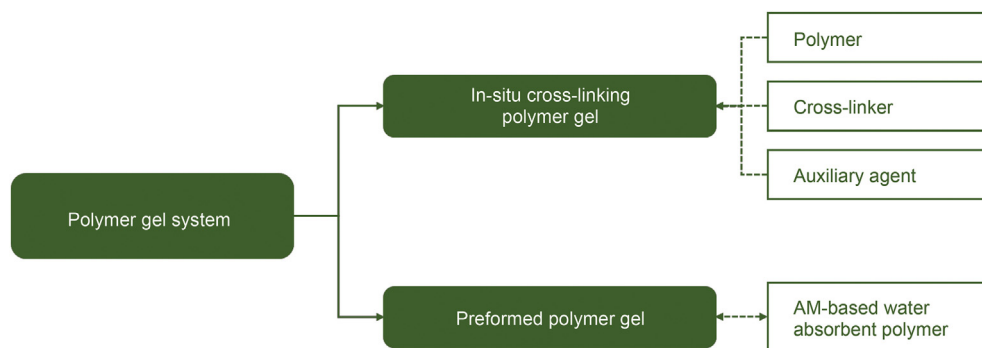


Fig. 3. NMR methods in polymer gel systems evaluation.

materials). Researchers found that ^{13}C and ^1H NMR technology can be applied to characterize the compositions of this kind of in-situ cross-linked polymer gel system. Besides, pre-formed gels are usually synthesized of acrylamide (AM) and other AM-based monomers in the surface facilities (Zhai et al., 2020; Zhu et al., 2021b). Therefore, ^{13}C and ^1H NMR have also been employed to evaluate the chemical structure and production yield of the synthetic samples.

3.1. Polymer characterization

3.1.1. Polymer chemistry structure characterization

The main skeleton structure of the polymer (e.g., HPAM, guar gum, and lignin) consists of carbon atoms. Through ^{13}C NMR analysis, the type of the functional groups on the polymer chains can be identified (Amaral et al., 2021; Bai et al., 2020; Juárez et al., 2020; Liu et al., 2019). PATBA is nowadays a very popular polymer used to produce high-temperature polymer gels; it can be reacted with polyethyleneimine (PEI) to form solid-like network structures in the formation. To study its gelation mechanisms with PEI, Al-Muntasheri (2008) used ^{13}C NMR techniques to characterize the chemical structure of PATBA. Fig. 4 shows the ^{13}C NMR spectrum of the raw PATBA product in the carbonyl region. Taylor and Nasr-El-Din (1994) found ^{13}C NMR could be the most suitable method to determine the hydrolysis degree of acrylamide (AM)-based copolymers after reviewing several suitable methods. To ensure 99% magnetization, Al-Muntasheri et al. (2006a,b) used a total recycle time that was longer than 5 times the carbonyl carbons relaxation

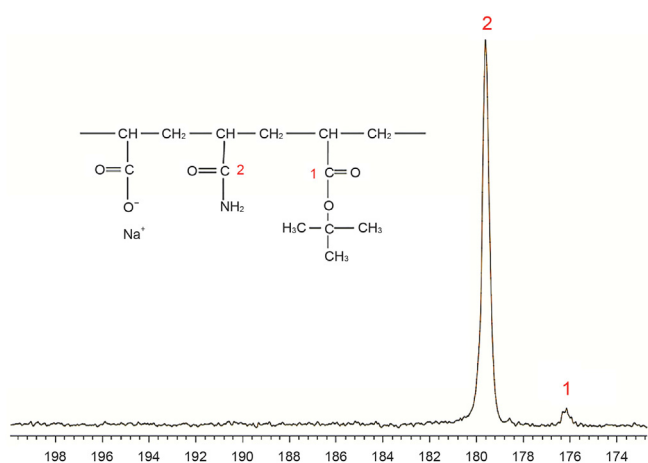


Fig. 4. ^{13}C NMR spectrum of the raw PATBA sample in the carbonyl region (Al-Muntasheri, 2008).

time and gave the following equations to determine the degree of esterification (E) and hydrolysis (τ), respectively (Al-Muntasheri, 2008):

$$E = \frac{(I_{\text{C=O}})_{\text{OC}(\text{CH}_3)_3}}{(I_{\text{C=O}})_{\text{OH}} + (I_{\text{C=O}})_{\text{OC}(\text{CH}_3)_3} + (I_{\text{C=O}})_{\text{NH}_2}} \times 100\% \quad (1)$$

$$\tau = \frac{(I_{\text{C=O}})_{\text{OH}}}{(I_{\text{C=O}})_{\text{OH}} + (I_{\text{C=O}})_{\text{OC}(\text{CH}_3)_3} + (I_{\text{C=O}})_{\text{NH}_2}} \times 100\% \quad (2)$$

where $(I_{\text{C=O}})_{\text{OC}(\text{CH}_3)_3}$ is the resonance peak intensity of the carbonyl carbon on the tBA group (176 ppm), $(I_{\text{C=O}})_{\text{OH}}$ and $(I_{\text{C=O}})_{\text{NH}_2}$ are the intensities of the carbonyl carbon at the carboxylate group (181–184 ppm) and the amide group (177–180 ppm), respectively. Based on these two equations, the esterification degree and the hydrolysis degree of the raw PATBA are 4.7 mol% and 0.1 mol%, respectively, which is very important for the analysis of the gelation mechanisms for the PATBA-PEI gel system and will be discussed in Section 3.1.2. Tessarolli et al. (2019) used ^{13}C NMR spectroscopy to characterize the chemical structure of copolymer synthesized by AA, AMPS and NVP. Moreover, the structural changes of reinforced polymer gels (e.g., reinforced PPG) can be characterized by ^{13}C NMR (Bai et al., 2021; Kumar et al., 2020).

In addition, as hydrogen atom is also an essential component of polymers, ^1H NMR is also usually employed to characterize the polymer chemical structure (Tian et al., 2020). Vargas-Vasquez et al. (2007b) found that the ^1H NMR T_2 curves of the HPAM particles (bulk samples) are bi-exponential. The results of the T_2 data analysis indicates that 97% of the ^1H NMR signal of the raw HPAM (Alcoflood 935) in response to the HPAM itself and the remaining 3% of the signal corresponds to the impurity. Luo et al. (2017) used ^{13}C and ^1H NMR to study the degradation performance of particle gels synthesized by AM, AA, and DMAM.

3.1.2. Gelation mechanisms related to changes of polymer chemical structures

Moreover, researchers have found that NMR information of different functional groups can help in calculating many critical basic characteristics (e.g., hydrolysis degree), which is useful for studying the gelation mechanisms of the in-situ cross-linking polymer gel systems (Ghriga et al., 2007). In addition, as the polymer is gradually reacted with the cross-linkers in the process of cross-linking, the T_2 relaxation time and the corresponding signal intensity of the carbon atoms in the polymer structures will change accordingly (Alhashim et al., 2018). Moreover, if the polymer system is cross-linked at elevated temperatures, the chemical structures of the polymer will change (e.g., thermal decomposition of polymers). Therefore, new signals (i.e., new functional groups on

the polymer chains) may be formed. For example, as mentioned in Section 3.1.1, the gel system composed of PAtBA and PEI has been widely studied by researchers for petroleum reservoirs with the temperature up to 80 °C (Morgan et al., 1998). The cross-linking mechanism put forward by Hardy et al. (1999) contains the generation of the covalent bond between the carbonyl carbon on the ester group of PAtBA and the imine nitrogen of PEI, as shown in Fig. 5. However, Reddy et al. (2003) proposed another mechanism in which the carbonyl carbon on the amide group of the polymer reacts with the PEI nitrogens by a transamidation reaction, as shown in Fig. 6.

To identify the gelation mechanisms of PAtBA with PEI, Al-Muntasheri et al. (2006a,b) examined the polymer structural changes of PAtBA using ^{13}C NMR spectroscopy. When the gelation process of PAtBA-PEI gel system is at temperatures lower than 100 °C and high pH, PAtBA will be hydrolyzed to produce HPAM and *t*-butyl alcohol, as shown in Fig. 7(a). This reaction mechanism was identified through the ^{13}C NMR. Two peaks observed at 30 and 70 ppm represented the methyl and tertiary carbons of the tertiary butanol, separately. Moreover, with the increase of the hydrolysis of the ester group, the tertiary butanol concentration increased (Shamlooh et al., 2020; Zhu et al., 2019). It took about 43 h to decrease the degree of esterification to zero, and no traces of *tert*-butyl acrylate was observed by ^{13}C NMR analysis. This can be a possible explanation for the long gelation time of this system at heating temperatures lower than 100 °C, which indicates the effectiveness of the gelation mechanism described in Fig. 5, where the gelation takes place by the nucleophilic attack of the imine nitrogen from the PEI on the carbonyl carbon of tBA group (Reddy et al., 2003; Vasquez et al., 2005). While for the cross-linking process of PAtBA-PEI gel system at the heating temperatures higher than 100 °C and high pH, Al-Muntasheri et al. (2006a,b) studied the relationship between the degree of esterification and aging time at 80 °C and 105 °C and found that the hydrolysis rate of the ester was nearly 7 times faster at 105 °C than that at 80 °C. Specifically, at the heating temperature of 120 °C, the tBA group was hydrolyzed entirely in 70 min only. Therefore, the formation of stable gels at elevated temperatures higher than 100 °C is obvious not the result of the gelation mechanism shown in Fig. 5. Hardy et al. (1999) showed that PAtBA would be thermalized at temperatures higher than 100 °C and high pH to generate HPAM and isobutene gas, as shown in Fig. 7(b). This result indicates that the mechanism in Fig. 6 is the mechanism controlling the cross-linking reaction when the heating temperature is higher than 100 °C. In this situation, the imine nitrogen of PEI attacks the polymer chain through the carbonyl carbon of the amide group (Zhu et al., 2019).

3.1.3. Influence of media (in bulk solution or porous media)

Whether they are in-situ cross-linked polymer gel systems or pre-formed gel systems, polymer and polymer gels will be pumped

into the reservoir (porous media), it is also imperative to determine the effect of the existence of porous media on the NMR signal and intensity of the polymer solution (Valiullin, 2016). Because there is a lot of water in the above two polymer gel systems, it is widely accepted to employ ^1H NMR method to study these polymer gel systems. Vargas-Vasquez et al. (2007b) found that all the ^1H NMR T_2 decay curves for HPAM solutions are mono-exponential. However, in the presence of the porous media, the fitting curve presents two clear-cut peaks: the right-hand peak represents the free polymer solution inside the biggest pores and the left-hand peak corresponds to the polymer solution in the smallest pore spaces, as depicted in Fig. 8. They found similarities in the T_2 measurements using the Berea sandstone.

3.2. Cross-linker

As we know, cross-linkers used in the compositions of in-situ cross-linked polymer gel systems can be divided into two main types. The first type is inorganic cross-linker, for example, aluminum chloride (AlCl_3), chromium acetate (CrAc_3), and zirconium acetate (ZrAc_4). The second type is organic cross-linker containing formaldehyde, phenol, phenolic resin, and polyethyleneimine (PEI). Because there are many hydrogen atoms in inorganic cross-linking (e.g., CrAc_3) solutions, analyzing the impact of the environmental medium by NMR T_2 analysis is also feasible (Kedir et al., 2014; Vargas-Vasquez et al., 2009). Moreover, for many special inorganic cross-linkers (e.g., aluminum Al^{3+}), ^{27}Al NMR analysis can be applied to determine the gelation mechanisms of the aluminum (Al^{3+}) cross-linked polymer gel systems (Lin et al., 2004).

3.2.1. Cross-linker chemistry structure characterization

For conventional inorganic cross-linkers (e.g., aluminum, Al, used to crosslinked with HPAM to form colloidal dispersion gels, CDG), ^{27}Al NMR technology can be employed to evaluate the reaction degree of Al with the reaction time. For PAM-aluminum gels, the release of Al^{3+} in the gelant is very crucial for its cross-linking reaction with HPAM, the ^1H NMR technique can be applied to study the pH dependency of aluminum citrate (Kedir et al., 2014). While here, we will focus on the characterization of some newly developed organic cross-linkers. For example, Wang et al. (2018b) developed a polyelectrolyte gelator for HPAM gels at low reservoir temperatures. To demonstrate the proposed generation process of the covalent bonds by the nucleophilic attack between the carboxylate group on the HPAM and sulfonium groups, spectra analysis of NMR combing rheological tests were provided. Moreover, to improve the mechanical stability of polymer gel systems during chase water flooding period, Wang et al. (2018a) also developed a kind of divinylbenzene (DVB) nanostructured cross-linker. This DVB nano-gelators have styrenyl groups, which was

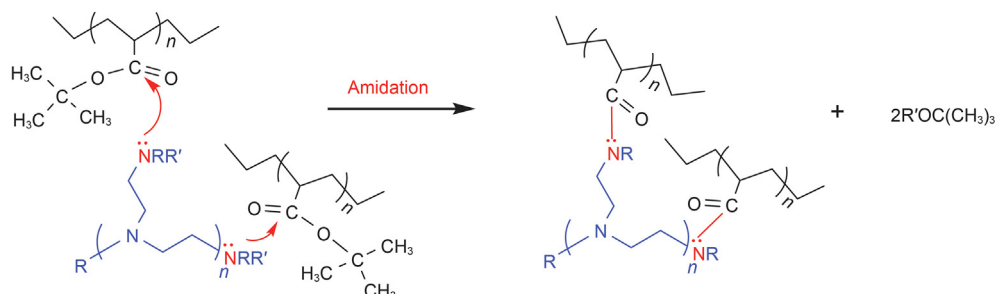


Fig. 5. Crosslinking reaction through ester carbonyl carbon (Hardy et al., 1999).

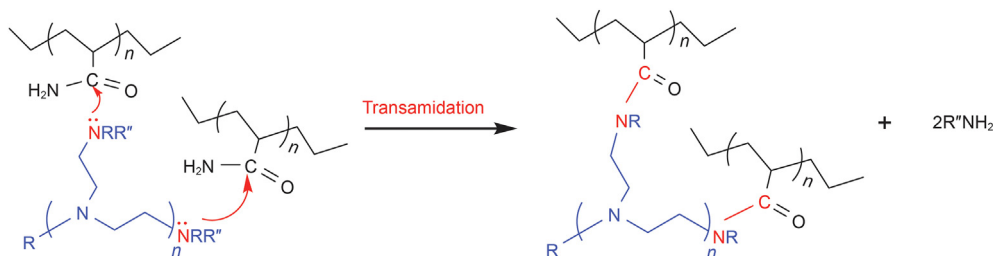


Fig. 6. Transamidation reactions between PAM containing amide pendant groups and nitrogen atoms of PEI (Reddy et al., 2003).

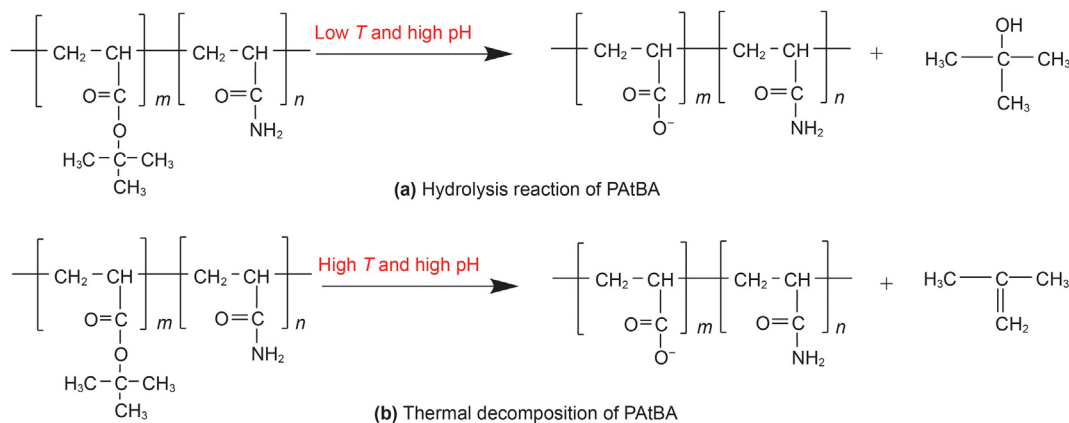


Fig. 7. HPAM transformed from PATBA (Al-Muntasheri, 2008; Al-Muntasheri et al., 2006a,b).

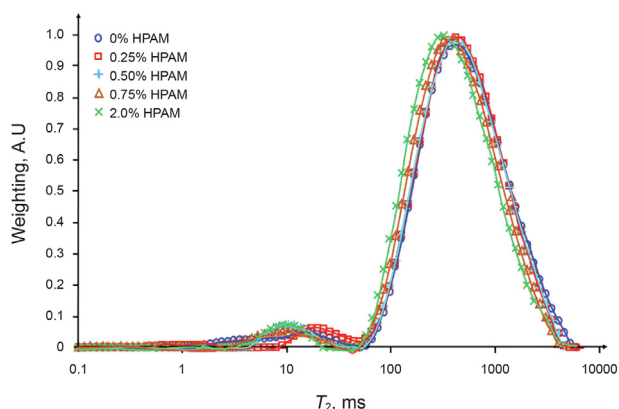


Fig. 8. T_2 distribution of polymer solutions in glass beads at 50 °C (Vargas-Vasquez et al., 2007b).

also manifested by NMR analysis.

3.2.2. Influence of media (in bulk solution or porous media)

The HPAM-Cr(III) acetate gel system has been developed by Sydansk and Argabright (1987) and widely studied and applied worldwide. In this system, the cross-linker (i.e., chromium acetate) in the formula is in the form of aqueous solution. Therefore, before analyzing the gelation mechanism of the in-situ cross-linked polymer gel system in porous media, it is critical to evaluate the influence of environmental media on the NMR signal distribution and intensity.

Through ^1H NMR technology, Vargas-Vasquez et al. (2007b) found that the T_2 decay curves of the bulk cross-linker solutions were mono-exponential in all situation, as shown in Fig. 9(a). In

addition, due to the paramagnetism of chromium(III), the ^1H NMR T_2 relaxation rate of the cross-linker solution increased with the increase in Cr(III) acetate concentration (Vargas-Vasquez et al., 2008). Therefore, there is an inverse correlation between T_2 and the concentration of Cr(III) acetate. This effect is called NMR paramagnetic relaxation enhancement, which is composed of the interaction between the magnetic moments of electrons and nuclei (Bakmutov, 2005). However, the T_2 measurements conducted in glass beads produced bi-exponential decay curves for the cross-linker solutions, wherein the concentration of Cr(III) acetate was less than or equal to 0.2 wt%, as shown in Fig. 9(b). The variation in cross-linker concentration also has a significant impact on the NMR T_2 of the cross-linker solution. The right peak in Fig. 9(b) represents the free cross-linker solution (with the concentration of 0–0.2 wt%) located in the biggest pores and the left peak corresponds to the Cr(III) acetate solution located inside the smallest pores. It is worth noting that the T_2 decay curve is mono-exponential when the Cr(III) acetate concentration was 0.3 wt%, which means that the influence of the paramagnetic properties of chromium(III) dominates the effect of surface relaxation on T_2 .

3.2.3. Gelation mechanisms related to cross-linker concentration analysis

As described in Section 3.2.1, NMR technology can be used to monitor cross-linker concentration over reaction time during gelation process (Vargas-Vasquez et al., 2008). For example, Lin et al. (2004) applied ^{27}Al NMR technology to evaluate the cross-linking mechanisms of the linked polymer solutions (LPS) composed of HPAM and aluminum citrate (AlCit). The spin-lattice relaxation time (T_{1i}) of aluminum in different cross-linked states during the reaction process of HPAM/AlCit LPS was measured. They found that T_{12} (represents the sol-state aluminum) does not change with the increase in reaction time; however, T_{11} (represents the

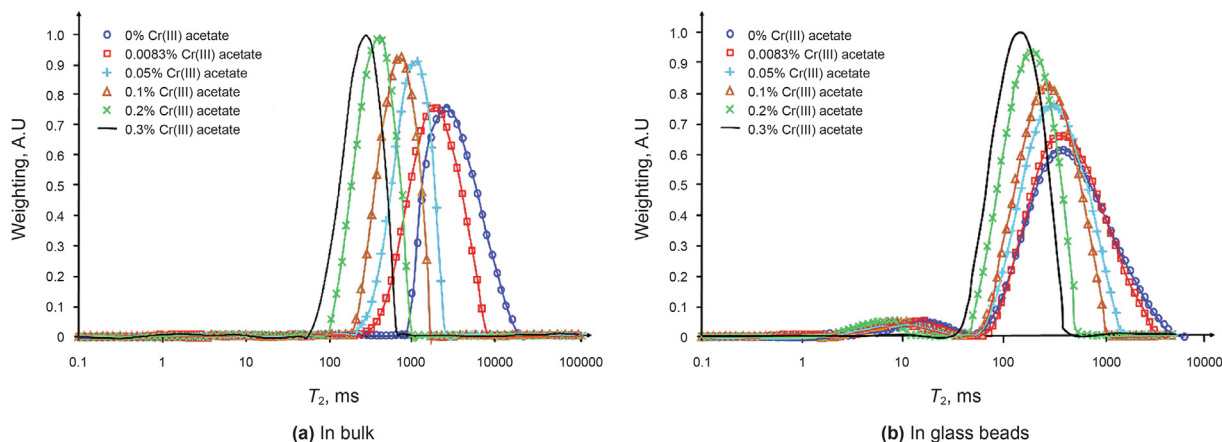


Fig. 9. T_2 distribution of cross-linker solutions in (a) bulk and (b) glass beads (Vargas-Vasquez et al., 2007b).

molecular-state aluminum) and T_{13} (represents the cross-linking-state aluminum) decrease. Which, in turn can explain the gelation mechanism that intramolecular cross-linking happens between HPAM and aluminum citrate, so the cross-linked polymer cluster shrinks and the molecular chain movement of the cross-linked polymer accelerates. Moreover, ^{13}C NMR technology can be applied to study the changes of ^{13}C -enriched formaldehyde in the HPAM-formaldehyde polymer gel systems with the aging time. Researchers found an 80-fold increase in the sensitivity for gel structures that consumed the formaldehyde (Fong and Kowalski, 1993).

3.3. Auxiliary agent

3.3.1. Oxygen scavenger

Vargas-Vasquez et al. (2007b) found that the addition of sulfite (e.g., 0.01 wt% Na_2SO_3) to the distilled water did not obviously affect the ^1H NMR bulk relaxation time (T_2) of distilled water. However, it is worth noting that this conclusion is derived from the NMR study of the HPAM-Cr(III) acetate gel system, the effect of the oxygen scavenger (e.g., sulfite and thiourea) on NMR T_2 of other polymer gel systems have not been reported yet.

3.3.2. Reinforcement material

Some reinforcement materials (e.g., nano- SiO_2 , nano- TiO_2 , and nano-clays) are usually added into the composition of the polymer gels to improve the gel strength. Conventional analysis method, such as Sydansk bottle test, viscosity measurement, rheometer test, and SEM, can provide the macroscopic property information of the gel system; however, it is very insufficient to analyze the reinforcement mechanisms. Zhao et al. (2014) employed low field NMR technology to study the chemical structure and gelation dynamics of the nanocomposite hydrogels synthesized of isopropyl acrylamide (NIPAM) monomer and lithium clay, which can be used as a kind of pre-formed gel system. It was found that the lateral relaxation time T_2 of the rigid phase changed slightly with the increase in clay content, which indicates that with the increase in the clay content, restricted polymer chains combined with the inorganic (clay) surface has not apparently changed. However, the T_2 of the solid phase was far less than that of the faster moving component, which shows that these polymers are nearly all combined with the inorganic (clay) surface. These results can indirectly reveal that fact that the polymerization process of the gel system happens on the surface of the clay (Haraguchi et al., 2005). It is worth noting that reinforcement materials (e.g., nano- SiO_2) have been employed in

the compositions of in-situ cross-linked polymer gel systems and widely studied in recent years; however, the reinforced mechanism has not been systematically studied and few results analyzed by NMR have been reported.

3.4. Pre-formed polymer gel

Pre-formed gels are another important types of polymer gels, and it is usually synthesized in the surface facilities. The pre-formed gels used for controlling conformance and improving oil recovery are typically AM-based copolymers (Zhu et al., 2017a; Zhu et al., 2021a). Therefore, before further evaluation of the performance of the polymer gel systems, it is important to verify the structure of its synthesis. Because pre-formed gels contain both carbon and hydrogen atoms in the polymer chains, it is suitable to employ ^{13}C or ^1H NMR method to analyze their structures. Taking the tetra-polymer gel as an example, the pre-formed gel was composed of acrylate (AA), AM, 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and [2-(acryloyloxy)ethyl]trimethylammonium chloride (DAC). Lai and Liu (2015) examined the product by ^1H NMR. The peak of 3.65×10^{-6} ppm is the proton peak of methylene chloride in the $-\text{SO}_2-\text{CH}_2-$ of the AMPS structure and the peak of 4.0×10^{-6} ppm is attributed to the proton peak of the methylene of $-\text{CO}_2-\text{CH}_2-$ of the DAC monomer. This above information shows that the synthesized product has the desired structure. Luo et al. (2017) also analyzed the structure of the designed pre-formed polymer gel by NMR spectroscopy and then study the degradation mechanism from the molecular structure changes.

4. Gelation performance characterization

For in-situ cross-linked polymer gel systems, the successful placement of the polymer gel system at a particular zone within the petroleum reservoir depends on the ability to forecast and change the gelation time and the final gel strength. Overestimation of the gelation time will cause the gel to cross-link prematurely in the wellbore while underestimating the gelation time will result in insufficient shut-in times. Gel strength is another important indication of the maximum pressure drop that polymer gels could withstand. Thus, the precise characterization of in-situ cross-linked polymer gel systems can provide the oil industry with the information needed to properly evaluate the gelation performance.

Usually, the gelation time and gel strength are determined using oscillatory rheology tests (Ghriga et al., 2019; Grattoni et al., 2001; Liu and Seright, 2001; Prud'homme et al., 1983; Reddy et al., 2003)

or bottle testing (Sydansk, 1988, 1990). Although rheology can quantitatively study the viscoelasticity of polymer gels and provide consistent gel descriptions, it is time consuming, expensive, and invasive (it can lead to a certain damage to the polymer gel structure). Moreover, rheology cannot measure the performance of polymer gels inside porous media. Bottle testing using the Sydansk's gel strength code method (Sydansk and Argabright, 1987), on the other hand, is practical and non-invasive and non-destructive. However, it is measured with the naked eye and, due to its qualitative nature, it may result in inconsistent and inaccurate gel description. Thus, to date, there has been no practical, accurate method available in the petroleum field to evaluate the gelation time and gel strength of in-situ cross-linked polymer gel systems. The EOR Laboratory at the University of New Brunswick has proposed a method for characterizing the in-situ cross-linked polymer gels through NMR technique (Vargas-Vasquez et al., 2007a, 2007b). NMR methods have the potential to give accurate information about the cross-linking process as they incorporate the critical quantitative feature of rheology with the non-invasive and non-destructive characteristics of bottle testing (Hirasaki et al., 2003; Vargas-Vasquez et al., 2007b). It can relate the gelation time and rheological storage modulus to the changes of transverse relaxation time (T_2) of the in-situ cross-linked polymer gel systems. In this section, the HPAM/Cr(III) acetate polymer gel will be selected for review because it has been widely studied and reported in the literature. Moreover, the HPAM/Cr(III) acetate polymer gel is suitable for ^1H NMR studies because of their high water content (usually up to 99.7 wt%).

4.1. Gelation time and gelation kinetic

There are three types of relaxation exist in a fluid: surface relaxation (T_{2S}), bulk relaxation (T_{2B}), and diffusion in the magnetic field gradient (T_{2D}) (McPhee et al., 2015). However, since fluid test samples are typically placed in a uniform magnetic field, only bulk fluids are measured, and the accelerated relaxation are negligible because of the diffusion effect in the magnetic field gradient. Therefore, the measured transverse relaxation is only because of the bulk relaxation (Bryan et al., 2003). Bulk relaxation (T_{2B}) is a fluid property that measures how easily the protons release energy to one another. It can be represented by the following equation (Bryan et al., 2003)

$$\frac{1}{T_{2B}} \propto \frac{\mu}{T} \quad (3)$$

where $1/T_{2B}$ is the bulk relaxation rate (s^{-1}), μ is the viscosity, and T is the absolute temperature. The bulk relaxation rate ($1/T_{2B}$) of a substance is directly proportional to its viscosity, i.e., a component with a higher viscosity relaxes faster than a component with lower viscosity. In this way, ^1H NMR measurements can be reproduced microscopically the macroscopically observed occurrences in viscosity measurements (Bryan et al., 2002).

Since the bulk relaxation rate of the gel sample is inversely proportional to the gel viscosity, the researchers found that low field NMR technology could be employed to evaluate the development of the polymer gel network and monitor the gelation kinetic. Alhashim et al. (2018) found that the T_2 amplitude peak of the polymer/HMTA/resorcinol gel shifted to left with varied aging time (i.e., shorter relaxation time T_2). To monitor the gelation kinetics, Romero-Zeron et al. (2008) studied the effect of polymer concentration and Cr(III) concentration on gelation time. When the PAM concentration in the gel composition increased from 0.5 to 1.5 wt%, the bulk relaxation rate ($1/T_2$) reduced, which is in proportion to the cross-linking rate and gel viscosity. However, the bulk

relaxation rate ($1/T_2$) increased when the HPAM/Cr(III) ratio decreased.

Romero-Zeron et al. (2008) also used ^1H NMR method to study the effect of salinity on gelation time. NMR spectra were taken about every 5 min from the starting of the gelation reaction evaluation (just after the mixing of HPAM and Cr(III) acetate). Fig. 10(a) shows the relationship between the bulk relaxation rate ($1/T_2$) of the polymer gel prepared in distilled water with different polymer concentrations and the reaction time. The liquid-solid transition for these systems can be defined by the linear interception point, which indicates a clear variation in bulk relaxation rate ($1/T_2$) versus reaction time (corresponding to a sudden increase in the gel viscosity). The liquid-solid transition point (i.e., the gelation time) for gels prepared by brine depicted in Fig. 10(b) is longer than those prepared in distilled water.

Al-Muntasheri et al. (2008) evaluated the effect of hydrolysis of HPAM on the gelation time of the in-situ cross-linked polymer gel system composed of HPAM and PEI. The degree of hydrolysis of different AM-based polymer products was tested by ^{13}C NMR spectrum and the viscosity changes of the polymer gel systems were measured as a function of reaction time. Results showed that with 7 wt% PAM (zero degrees of hydrolysis), the gelation time with 0.3 wt% PEI was about 2 h because PAM can gradually hydrolyze in an alkaline environment and generate carboxylate groups and ammonia (Kurenkov et al., 2001). However, the gelation time decreased to 0.55 h when an HPAM with an origin hydrolysis degree of 4.7 mol% was employed.

Since the continuing buildup (macro-performance is increased viscosity) of the polymer gel network can be seen from the bulk relaxation rate ($1/T_2$) curves, as shown in Fig. 10, the bulk relaxation rate ($1/T_2$) can correspond to the rate at which the cross-linker is crosslinked with the polymer molecules. Therefore, it is possible to associate the bulk relaxation rate ($1/T_2$) and the polymer or the cross-linker concentration to estimate the gelation rate law (i.e., gelation kinetics) of the gelation process of in-situ cross-linked polymer gel systems (Alhashim et al., 2018). Romero-Zeron et al. (2008) demonstrated that the variation of the normalized bulk relaxation rate ($1/T_2$) with reaction time could fit a straight line and the cross-linking reaction between HPAM and CrAc_3 at 30°C abides by a second-order rate law. Additionally, activation energies for the crosslinking reaction can be determined through the Arrhenius-type law. Although these results matched with those reported in the literature (Prud'homme et al., 1983; Sydansk, 1988; te Nijenhuis, 2001), more research is still needed, in our opinion, to systematically study the relationship between the bulk relaxation rate and the gelation kinetic (i.e., the gelation time) under different influencing factors, for example, high-temperature conditions. Moreover, NMR measurements does not disrupt the gel structure during test, so the gelation time might be different (usually shorter) from those measured by bottle tests (Alhashim et al., 2018).

4.2. Gel strength

Bottle testing method is a highly qualitative method which uses the visual consistency. Therefore, oscillatory rheology is suggested to characterize gel strength because it can offer better reproducibility of the complex viscosity (η^*) measurements for polymer gel systems (Kakadjian et al., 1999). However, researchers discovered that dynamic rheology testing is an invasive method that would cause some damage to the gel network and cannot characterize the performance of the polymer gel systems in porous media (Chauveteau et al., 1997; Kakadjian et al., 1999; Prud'homme et al., 1983; Reddy et al., 2003). In recent years, low field NMR technology is employed to study the gel strength.

Vargas-Vasquez et al. (2007a) provided the relaxation time (T_2)

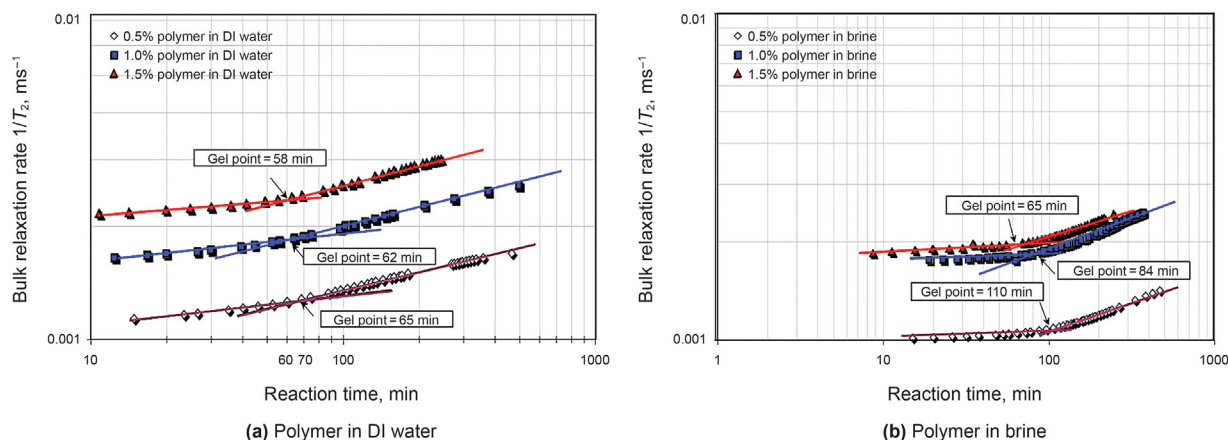


Fig. 10. The relationship between bulk relaxation rate ($1/T_2$) of the polymer gels prepared in (a) distilled water and (b) in brine and reaction time. The experiment was conducted at 30 °C, with an HPAM-to-Cr(III) acetate ratio of 40:1. The concentration of HPAM solution varied between 0.5 and 1.5 wt% (Romero-Zeron et al., 2008).

changes in both Cr(III) acetate and the polymer gel composed of 0.75 wt% HPAM and 0.3 wt% Cr(III) acetate at 40 °C. Results showed that T_2 of the polymer gel system reduced in the first 5 h and leveled off after that. The increasing of the complex viscosity (η^*) of the polymer gel would gradually restrict the motion of H species and thus reduces the relaxation time. They also found that the complex viscosity (η^*) and the bulk relaxation rate ($1/T_2$) changed as a function of the reaction time before reaching the gelation time, moreover, both curves had similar trends, as shown in Fig. 11. Therefore, they claimed that ^1H NMR could monitor variations in the polymer gel before reaching the gelation time. It is worth noting that although ^1H NMR cannot monitor variations in gel strength after reaching the gelation time, this technique can provide quantitative results that can be related to rheological properties without damaging the gel network. However, Romero-Zeron et al. (2008) claimed that the bulk relaxation rate appears to qualitatively correlate with the complex modulus (G^*) instead of the complex viscosity (η^*). Therefore, more ^1H NMR investigations should be carried out for other different polymer gels formula to obtain an enhanced relationship between bulk relaxation rate and complex viscosity for in-situ cross-linked polymer gel systems.

4.3. Gel syneresis

Syneresis is one of these chemical modifications and it will

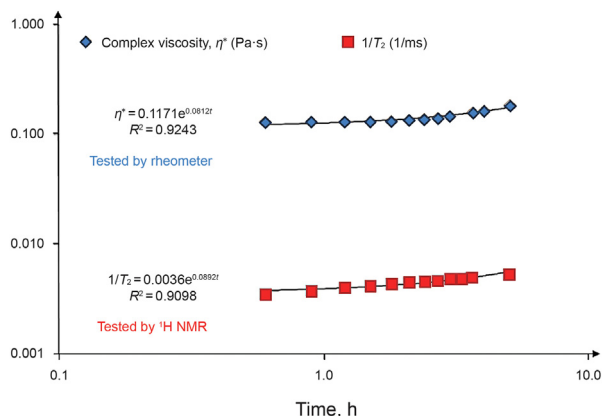


Fig. 11. Comparison between complex viscosity (η^*) and T_2 values with different aging times after polymer gel formulation at 40 °C (Vargas-Vasquez et al., 2007a).

cause the gel to shrink in volume, and consequently, water is squeezed out of the gel structure (Karimi et al., 2016; Vossoughi, 2000). Moreover, gel syneresis is strongly affected by polymer and cross-linker concentrations, solution salinity and pH, and heating temperature (Bryant et al., 1997; Vossoughi, 2000; Xiong et al., 2018). Romero-Zeron et al. (2008) observed the starting and the syneresis process of the HPAM/Cr(III) acetate gel system as a function of time. Both low field NMR measurement and direct observation by bottle testing were employed. When the HPAM-to-Cr(III) acetate ratio increased to 5:1, the bulk relaxation rate ($1/T_2$) reduced gradually with time after 120 h of aging, which means the starting of gel syneresis. These lower values of bulk relaxation rate ($1/T_2$) are concerning with the emergence of two phases: shrunk gel and free water. Fig. 12 shows normalized amplitude and reaction time as a function of relaxation time (T_2) for the HPAM/Cr(III) acetate gel system. The dashed curves with open symbols represent the amplitude baselines of standard solutions of chromium acetate and polymer solution in brine. The thick darkest curve represents the gel just after polymer and Cr(III) acetate mixing. Departing from the locations of the standard baselines and fresh gel curves, it is possible to observe the chemical modifications that the gel endures with time. After 4 days of gelation, the square-symbol curve shows the migration of the amplitude peak to the left. This indicates the formation of a viscous gel network because the signal shifts toward lower bulk relaxation rates. However, after 9 days of aging, the gel sample displays two amplitude peaks. One peak gradually moves to the left (corresponding to a lower relaxation time), and the other peak is at a higher relaxation time. Currently, the gel presents syneresis and two well-defined phases are evident from the NMR spectra: a solid network structure and an aqueous solution. In addition, the syneresis progressed after 24 days of aging.

5. Gelation performance and fluid flow behavior in porous media

5.1. Oil recovery and residual oil distributions caused by polymer gel treatments

There are three most popular visual oil displacement techniques: etched model using the microscopic techniques, CT technology, and nuclear magnetic resonance imaging (MRI) technology. Observing the fluids (e.g., oil, water, polymer gel) behavior in an etched model or sandpack using the microscopic technique is one of the popular methods to study the microscopic profile improvement and water shutoff mechanisms of polymer flooding and

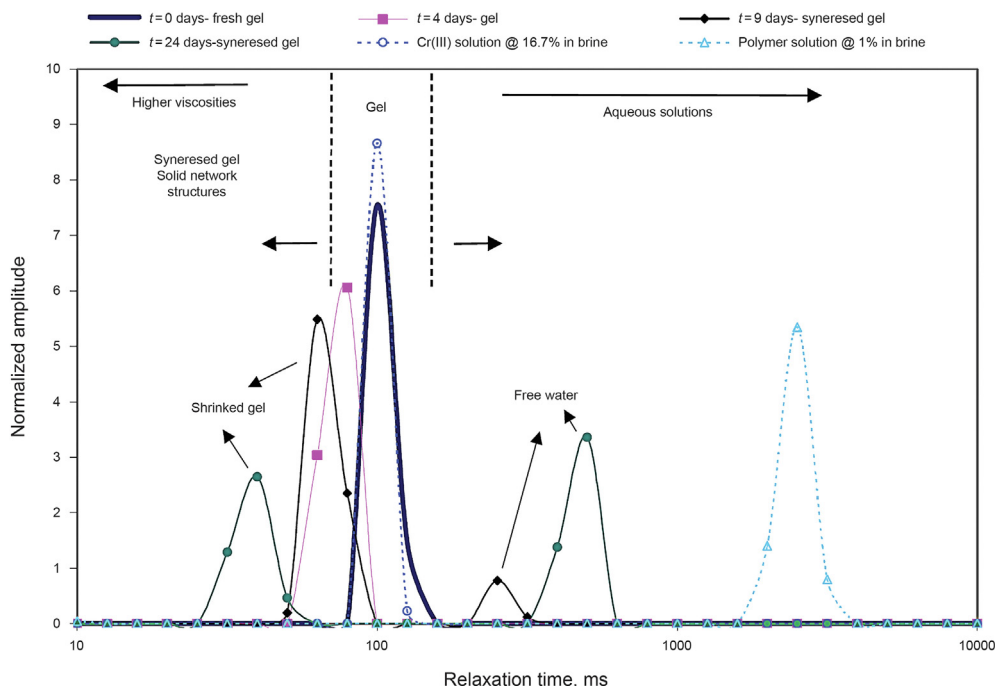


Fig. 12. Amplitude index versus relaxation time. The dashed curves with open symbols indicate the standard solutions of 1 wt% polymer solution and 16.7 wt% of chromium acetate in brine. The polymer gel system was formulated with 1 wt% HPAM and with an HPAM-to-Cr(III) acetate ratio of 5:1, and the experiment was conducted at 25 °C (Romero-Zeron et al., 2008).

polymer gel conformance improvement. However, this microscopic displacement method mainly relies on optical microscopy, which requires the tested samples to have a certain light transmission (i.e., the thickness of the simulated porous media should be less than 3 mm). CT technology can quantitatively evaluate the petrophysical properties of the porous media and visually characterize the rock pore structure. However, when there are several fluids, it is difficult to distinguish the images between the fluids and the porous media skeletons. Since the (manually adjusted) relaxation times T_2 of crude oil, water, and polymer gels in the reservoir porous medium are usually different, as shown in Table 1, nuclear magnetic resonance (NMR) technology can be employed to analyze different types of fluids in the microscopic pore structure of the reservoir by only collecting the signal of the fluid (Alshehri et al., 2019b; Gaol et al., 2020; Li et al., 2020; Liang et al., 2007; Yuan et al., 2019). Therefore, the state of existence and the influencing factors of the

movable fluids before and after the polymer gel treatments can be studied.

Table 2 shows the gel treatment performance and fluid behavior analysis of different researchers applying NMR technology to different polymer gel systems in recent years. Zhou et al. (2005) combined the NMR visualization technology with the traditional core flooding experiments to analyze the propagation characteristics of weak gels without oil in the core. The weak gel system was formed by crosslinking HPAM and phenolic resin and was prepared from heavy water (D_2O) that cannot be detected by NMR. Since the relaxation times (T_2) of water and oil have overlapping parts, the NMR spectrum and images of the two fluids cannot be distinguished. Therefore, the NMR signal of water and oil was distinguished by using 0.5 wt% $MnCl_2$ aqueous solution, and the weak gel system was prepared by using D_2O so that the NMR signal cannot be detected, and thus the NMR signals of the polymer gel and the

Table 1
Treatments for different fluids for polymer gel core flooding tests in porous media.

Fluid	Treatment	Mechanism	Reference
Water	Treated with manganese dioxide ($MnCl_2$)	Distinguish the signals between water and oil. Mn^{2+} in $MnCl_2$ aqueous solution is only in contact with H protons in water not H protons in oil.	Zhou et al. (2014) Shang et al. (2002)
	Treated with heavy water (D_2O)	Distinguish the signals between water and oil. D_2O has no NMR signal	Kang et al. (2019) Ramskill et al. (2018)
Oil	Treated with fluorine	Distinguish the signals between water and oil. Hydrogen nuclei in oil are entirely replaced by fluorine to shield the oil signal.	Liang et al. (2018)
	Dehydrogenate kerosene	HPAM/Cr(III) gelant is sensitive to $MnCl_2$. Dehydrogenate kerosene is invisible by NMR	Zhou et al. (2014)
Polymer gel	Treated with heavy water (D_2O)	Distinguish the signals between gel and oil. When using heavy water (D_2O) to prepare a weak gel solution, it has no NMR signal, but for crude oil the signal can be detected.	Zhou et al. (2005)

Table 2
Applications of NMR technology to gel treatment performance and fluid behavior analysis of different polymer gel systems.

Polymer gel system	NMR applications	Core samples	Reference
PAM-chromium gel	Oil recovery improvement	Heterogeneous carbonate composite core	Alshehri et al. (2017)
PAM-chromium gel	Sweep efficiency improvement	Fractured carbonate core	Kwak et al. (2017) Alshehri et al. (2018) Alshehri et al. (2019b)
PAM-chromium gel	Disproportionate permeability reduction mechanism	Homogeneous sandstone core	Liang et al. (2018)
HPAM-phenolic resin gel	Distribution changes of residual oil saturation	Homogeneous sandstone core	Zhou et al. (2005)
Polymer microspheres	Plugging mechanism	Homogeneous sandstone core	Yi (2013)
	Displacement efficiency		Pu et al. (2018) Nie et al. (2019) Du et al. (2020b)
Preformed particle gels (PPG)	Enhanced oil recovery mechanism	Heterogeneous sandstone core	Kang et al. (2019)
Poly(ethylene glycol) (PEG)-1 gel particles	Plugging performance	Homogeneous sandstone core	Gao et al. (2020)

oil can be differentiated. NMR sagittal and transverse imaging was performed during the whole displacement process. Variations of T_2 spectra and residual oil saturation during weak gel flooding was also studied (Zhou et al., 2005), as shown in Fig. 13. The peak of the T_2 spectrum in Fig. 13(a) represents the NMR signal of the oil phase. With the continuous pumping of the displacement agent, the peak area gradually decreases, indicating that the oil saturation in the core gradually decreases, which shows that the weak gel system exhibits a good oil displacement efficiency. After the injections of polymer and water, the summit of the T_2 peak is slightly shifted to the right compared to the first water flooding, and the summit shift after weak gel injection is more obvious, indicating that the accumulation of oil droplets becomes larger. The NMR transverse and sagittal images of residual oil distributions after displacement are shown in Fig. 13(b) and (c). There is almost no residual oil near the inlet of the core, and some isolated oil-bearing areas are formed in the middle of the core. Some strip-shaped areas are formed near the outlet, which further proves that the system has better oil displacement effect.

Shang et al. (2002) employed MRI technology to evaluate the profile control performance of high-temperature polymer gel system. Water was first injected into a heterogeneous core after steam flooding (250 °C), and then a $MnCl_2$ aqueous solution was injected to observe the heterogeneity of the core. Finally, high-temperature plugging agent was injected into the core and aged at 60 °C, MRI images show that most of the plugging agent can propagate into higher permeability porous media and have an excellent plugging performance. Yi (2013) studied the effect of profile modification of

polymer microspheres in porous media with different permeabilities through laboratory flooding experiments and NMR experiments. Results from the core flooding experiments combining NMR analysis showed that the particle size of the polymer microspheres should match the pore throat size. Kang et al. (2019) studied the enhanced oil recovery mechanism of PPG treatment in the heterogeneous core by NMR technology and core flooding experiments. PPG can plug the large pore throats and displace the remaining oil during the subsequent water flooding period. Alshehri et al. (2017) used low-field NMR techniques to study the conformance control performance of PAM-chromium gels in carbonate cores. D_2O was applied to replace water and results showed that the bypass oil can be effectively recovered after polymer gel treatment. They also found that the sweep can be improved and manifested by NMR techniques (Alshehri et al., 2018; Alshehri et al., 2019b).

For other improving oil recovery (IOR) methods, NMR and MRI techniques have been widely applied to monitor the changes of residual oil distributions (Kwak et al., 2019; Mangane et al., 2017); however, literature about the NMR technology used for profile control and water shutoff is not much, more work should be done to strengthen this technology.

5.2. Disproportionate permeability reduction (DPR) effect of polymer gels in porous media

To study the mechanism of the disproportionate permeability reduction (DPR) effect of polymer gels at the pore level, Liang et al.

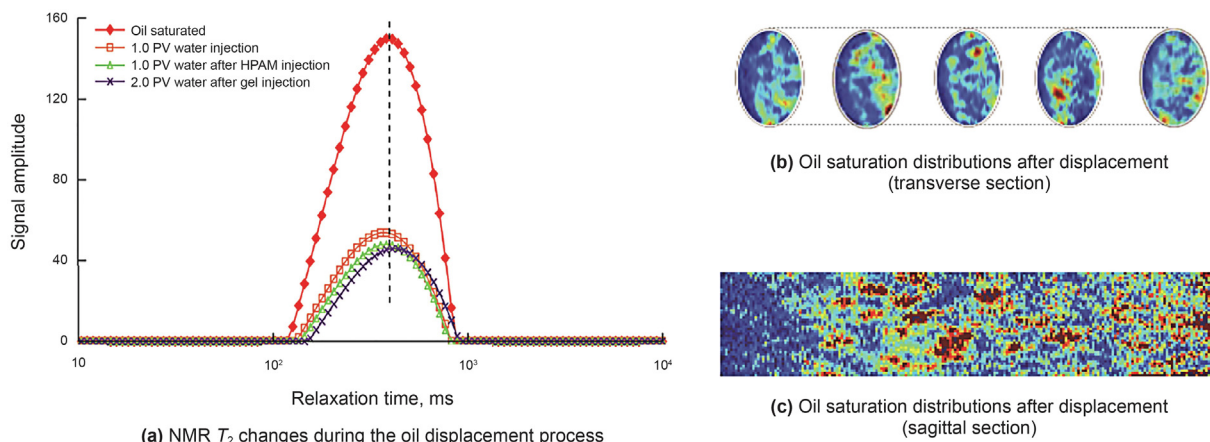


Fig. 13. Variations in T_2 spectra and residual oil saturation distributions during weak gel flooding. The core has a water permeability of 1.488 D, a diameter of 2.5 cm, and a length of 8.98 cm. Water was a 0.5 wt% $MnCl_2$ aqueous solution, oil was diesel oil, and the weak gel was an HPAM/phenolic resin gel system prepared by heavy water (Adapted from Zhou et al. (2005)).

(2018) used the NMR scanning technique for his core flooding experiments, in which the oil and water core-flooding processes were scanned by NMR. This scanning reflects the change of phase saturation, which helps to understand the change behavior of oil and water flow pathways. The gel system was composed of 0.3 wt% HPAM, 0.4 wt% Cr(III) acetate and 0.3 wt% NaCl. The NMR results at different injection times are depicted in Fig. 14. For example, Fig. 14(a) shows that when the oil injection amount reaches 7 PV, the signal in the large pores decreases sharply (notably, the fully fluorinated oil used in the experiment has no NMR signal), while the NMR signal in the small pore increases first and then decreases. It can be determined that the gel in the pore is gradually displaced by the chase oil. Therefore, the gel displacement mechanisms are the primary reasons for the original oil-pathway development in large pores, as shown in Fig. 15(a) illustrated by Seright et al. (2002). Moreover, when chase water was injected, the permeability reduced from 0.5 to 0.04 Darcy, high residual oil saturation and gel rehydration are two principal mechanisms for the DPR to water, as also depicted in Fig. 15(b). This can also be manifested by the NMR results, the signal amplitude in both large and small pores recover significantly. However, more studies for other polymer gel systems should be studied to verify the feasibility and utility of the NMR technique. It is worth noting that the DPR mechanism of polymer gels also includes the alteration of adsorption and wettability, and the existing studies on this aspect of NMR in gels have been reported. The mechanistic studies on the alteration of wettability in other oil repellent systems (e.g. nanoparticle oil repellent systems) have been investigated (Zhou et al., 2019), so the subsequent studies can be used as a reference to further enhance the NMR

technique in the DPR mechanism of polymer gels. For more details about the experiments and explanation, please read the reference published by Liang et al. (2018).

Alshehri et al. (2019a) studied the viscosity and divergence effects of chromium (III)/polymer gel treatments in fractured cores by NMR measurements. Gao et al. (2020) used the nuclear magnetic resonance technology and flooding experiments to study the plugging effect of the poly(ethylene glycol) (PEG)-1 gel particle system in pore spaces at different scales. Pu et al. (2018) found that DPR effects occurred during polymer microspheres (PM) flooding. PM injected could shift the oil-water isotonic point into higher water saturation, leading to the generation of convex shape in the relative permeability curve of water. However, literature about DPR effect analyzed by NMR technique increases in recent years but still limited (Al Hashim et al., 2020; Chen et al., 2020). Therefore, more work should be done to consolidate and verify the feasibility of NMR technology in the above DPR mechanism analysis of different gels.

6. Discussion and prospects

Based on the literature reports and their vacancies or deficiencies (see Table 3), the following suggestions and research prospects for NMR technology in the fundamental performance evaluation of water control and oil improvement performance of the polymer gel system are presented.

For the in-situ cross-linked polymer gel systems, most of the studies still focus on the HPAM/Cr³⁺ gel system, and there are very few reports about the high-temperature polymer gel systems, for

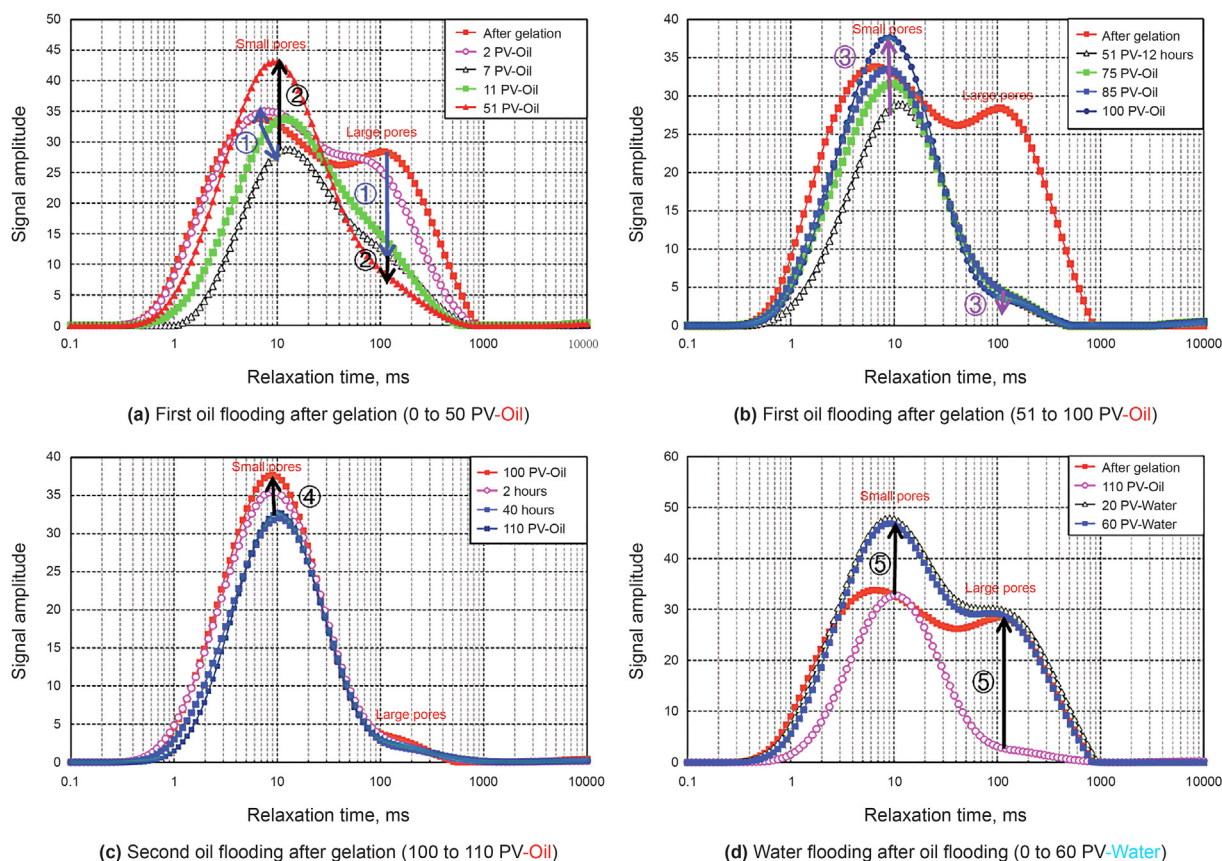


Fig. 14. NMR T_2 scanning curves at varied injected pore volumes (PV) in the core with the permeability of 2.3 D: (a) 0 to 51 PVs of oil, (b) shut-in for 12 h and 51 to 100 PV of oils, (c) shut-in for 40 h and 100–110 PVs of oil, and (d) 0 to 60 PVs of water injection (Adapted from Liang et al., 2018).

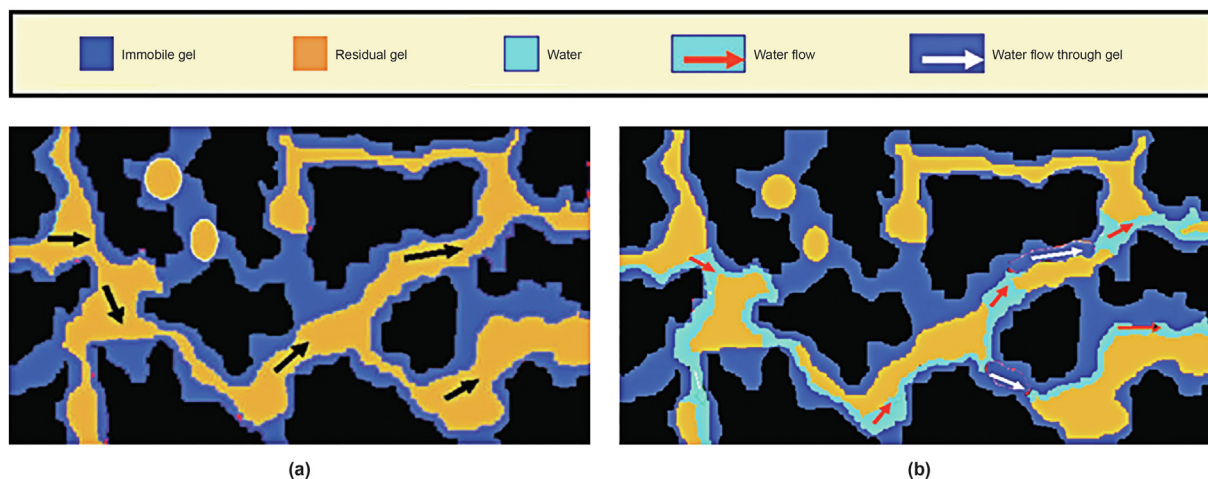


Fig. 15. Schematic diagram of the mechanisms causing DPR: (a) oil open channels by dehydrating the gel and (b) water propagation following oil flood after gel placement (Adapted from Seright et al., 2006).

Table 3
Summary of the current applications of NMR technology in polymer gel characterizations.

NMR type			Conventional NMR	Low field NMR	MRI
In-situ cross-linked polymer gels	Gelling system characterization	Chemistry structure	PAtBA Aluminum crosslinker Formaldehyde crosslinker Newly designed organic crosslinker	Auxiliary agent	/
		Influence of porous media	/	HPAM solution Cr(III) solution	/
	Gelation performance		Gelation time (HPAM-PEI gel system)	Gelation time (HPAM-Cr gel system) / Gelation strength (HPAM-Cr gel system)	
	Gel performance in porous media		/	Gel syneresis (HPAM-Cr gel system) Gel propagation (HPAM-phenolic resin gel system) DPR effect (HPAM-Cr gel system)	Gel propagation (HPAM-phenolic resin gel system)
Preformed particle gels	Gelling system characterization	Chemistry structure	AM-based preformed gels	Not found	/
	Gel performance in porous media		/	Not found	Not found

example, the HPAM/phenolic resin gel systems and the HPAM/PEI gel systems. As we know, their gelation mechanisms are forming a covalent bond by dehydration condensation between the polymer acrylamide group ($-\text{CONH}_2$) and the hydroxyl group (e.g., phenolic resin) or the imino group (e.g., PEI). They are totally different from the weaker coordination bond between the carboxyl group ($-\text{COOH}$) of the polymer and the metal crosslinking agent (e.g., chromium acetate). In addition, the metal ions (e.g., Cr^{3+}) in the metal cross-linking agent generally have a specific paramagnetic property, which may interfere with the NMR test results. Therefore, these high-temperature polymer gel systems should be systematically studied and then compared with the HPAM/ Cr^{3+} system. This, on the one hand, will help to further expand the application of NMR technology in the evaluation of polymer gel systems, and on the other hand, it will help to verify the feasibility of NMR technology in polymer gel evaluation.

In addition, combining the advantages of NMR detection technology, such as no damage to the test samples and useful measurement in porous media, etc., the (static or dynamic) gelation mechanism, the shear degradation mechanism and dehydration mechanism of the in-situ crosslinked polymer gel system in porous media could be further studied. It is worth noting that the current gelation mechanism analysis of the in-situ crosslinked polymer gels

is usually studied in ampoules, viscometers or rheometers (i.e., in bulk). The gelation mechanism in small pore throats has rarely been reported.

For the pre-formed polymer gel systems, in addition to continuing to use NMR technology to detect newly designed crosslinkers or pre-formed polymer gels, it is also possible to study the propagation characteristics of pre-formed polymer gel systems in porous media and the plugging and oil displacement effect under different operation conditions. For example, evaluations of the plugging effect and degradation performance of PPG under carbon dioxide conditions, etc. By these, the current theories that are not very mature about the pre-formed polymer gel systems for improving oil recovery should be supplemented and improved.

Last but not the least, the matching relationship between the NMR techniques and other conventional polymer gel evaluation techniques (such as Sydansk bottle test, viscosity method, and rheological test) needs further research and verification. For example, when Romero-Zeron et al. (2008) studied the in-situ cross-linked polymer gel system (the HPAM/ Cr^{3+} gel system), they found that the gelation time obtained by NMR technique was similar to that obtained by the rheological test, but the gelation time obtained by the Sydansk method was entirely different. They claimed that the signal intensity of this polymer gel system

detected by spin-echo MRI might be related only to the early stage of the cross-linking reaction between HPAM and Cr(III) acetate. In addition, Vargas-Vasquez et al. (2007a) found that there was a good matching relationship between the gelation strength measured by NMR technology and the complex viscosity (η^*) measured by the rheometer; however, Romero-Zeron et al. (2008) believed that there should be a better matching relationship with the complex elastic modulus (G^*). Moreover, they did not give the corresponding gel strength quantitative test results. Therefore, the relationship between these three methods needs to be further unified. Therefore, two or more methods should be combined to evaluate and monitor the gelation performance. In addition, the action mechanism of polymer gel in porous media is very important for its EOR design in the oil field. However, this point has not been fully studied by NMR technology, such as the influence of different oil-water saturation, permeability difference, cracks, profile control agent slug combination, etc. on the effects of DPR and EOR. In the follow-up, we can make understanding of the mechanism that NMR technology can provide in the research related to EOR design.

7. Conclusion

Based on the existing literature, we reviewed the application of NMR technology in polymer gel systems for controlling conformance and improving oil recovery. This paper reviews four aspects, namely, gel system characterization, gelation performance characterization in bulk, gel performance and fluid flow behavior analysis in porous media. Since the in-situ cross-linked polymer gel system consists mainly of C and H atoms, the polymers and crosslinkers (especially their functional structures) can be characterized using ^{13}C or ^1H NMR techniques. In addition, for metal cross-linking agents (such as aluminum), ^{27}Al NMR techniques can be used to monitor the change of the relaxation time in the gelation process to reveal its gelation mechanism. The functional structures of the newly synthesized pre-formed polymer gels can also be characterized by ^1H and ^{13}C NMR techniques. The low-field ^1H NMR technique can be used to evaluate the gelation time, gel strength and dehydration performance of the in-situ cross-linked polymer gel system. In addition, NMR technology has a great perspective to be used to monitor the gel conformance improvement effect as it has already been successfully applied to monitor the changes of fluid saturation, porosity, and permeability, etc. in the formation. Although the application of NMR technology in polymer gel system evaluation is still not mature, this review can provide a new insight for petroleum research and engineers to better understand the NMR technology in the field of polymer gels for controlling conformance and improving oil recovery.

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