Synthesis and Properties of Branched Polymer Based on Modified Chitosan for Enhanced Oil Recovery

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Abstract. In this study, chitosan and poly amide-amine(PAMAM) were utilized to prepare a branched polymer based on modified chitosan (HPDCS) for enhanced oil recovery (EOR). The structure of the product was confirmed by FT-IR, ¹HNMR and SEM. Compared with hydrolyzed polyacrylamide (HPAM), HPDCS exhibited better thickening properties and shear resistance due to its special branched structure and the flexible molecular chains can be deformed through the pore throat of the porous medium, which can avoid serious damage to the molecular chains. After a 45-hour reaction period with biological enzyme, the apparent viscosity of the HPDCS solution decreased significantly, and the viscosity retention rate was only 67.7%, indicating that the introduction of chitosan in the polymer could improve the biodegradability of polymers to a certain extent. Based on sandpacked tube displacement experiments, the HPDCS could build high resistance factor and residual resistance factor in the corresponding porous medium which indicated that the HPDCS performed excellent mobility control ability. Besides, compared with HPAM, the HPDCS solution of 2000 mg/L showed better oil recovery of 24.12% in the corresponding porous medium, which demonstrated that the branched polymer has a more outstanding EOR ability.

1. Introduction
Hyperbranched polymers are a new class of polymer having a specific structure and properties. Compared with linear polymers, they have a highly branched, three-dimensional structure, a large number of terminal functional groups properties, high chemical reactivity, good solubility, etc [1]. In our previous studies[2-4], introducing a hyperbranched structure into a polymer flooding agent was proposed. The hyperbranched polymer had more branches, with modified nano-SiO₂ and PAMAM, as the cores respectively were developed. Such polymers have a stronger resilience and shear deformation ability, and core flooding experiments show that hyperbranched polymers in porous media can establish a higher flow resistance and improve the sweep efficiency of the displacement fluid and have excellent EOR ability.

As oil development moves toward low-carbon, environmental protection, the polymer in oil fields needs economy, efficiency, and green eco-friendly performance and biocompatibility. Increasing
interest has been generated in smart polymers based on natural polymers, such as polysaccharides. Chitosan (CS), is a partially or fully deacetylated chitin product, which is widely found in crabs, shrimp, other crustaceans, algae, and in other marine organisms. Various methods have been proposed to prepare a water-soluble chitosan derivative for the purpose to expand its scope of application. Currently, the chitosan modification technology is mainly alkylation, acylation, carboxylation, quaternization, and graft copolymerization, etc[5-6].

In this work, we synthesize a branched polymer based on modified chitosan for enhanced oil recovery with excellent shear resistance and biodegradability. For this purpose, we first prepared N-maleated chitosan by the acylation process. Afterwards, PAMAM dendrimers were grafted onto N-maleated chitosan by acylation reaction accelerated by N-hydroxysuccinimide (NHS) and 1-Ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC). Then we introduced an unsaturated double bond into N-MACS-graft-PAMAM to synthesize a modified dendritic chitosan functional monomer (DCS). The branched copolymer (HPDCS) was obtained by the free radical copolymerization of acrylamide (AM), acrylic acid (AA), and the DCS. Characterizations, including FT-IR, 1H-NMR, SEM, and water-solubility determined by solution turbidity measurement, were performed to investigate the product’s structures and properties. And branched copolymer’s thickening performance, shearing resistance properties, biodegradability, injection property, mobility control ability and EOR ability were further explored.

2. Preparation of the branched polymer HPDCS

2.1. Preparation of dendritic chitosan functional monomer
Chitosan (CS) which contains a lot of -NH₂, is a rare natural polymer with a positive charge and has a unique structure and unique activity [7-8]. Firstly, the CS was N-maleated, thus improving the performance of CS dissolved in some organic solvent, to facilitate the subsequent reactions [9]. And then PAMAM dendrimer was grafted onto N-maleated chitosan (N-MCS) by acylation reaction accelerated by NHS/EDC to get N-MCS/PAMAM. Then we introduced an unsaturated double bond into N-MACS/ PAMAM to synthesize a modified dendritic chitosan functional monomer (DCS). Synthesis principle shown in figure 1.

![Figure1. Synthesis route of dendritic chitosan functional monomer (DCS).](image-url)

2.2. Preparation of the branched polymer HPDCS

By free-radical aqueous solution polymerization, the dendritic chitosan functional monomer (DCS) and acrylic acid (AA), acrylamide (AM) were copolymerized to obtain branched polymer HPDCS (figure 2). The copolymerization conditions are presented in table 1. And by Ubbelohde viscometer, the polymer’s viscosity average molecular weight was calibrated, about $2.94 \times 10^6$.

![Figure 2. Synthesis route of branched polymer HPDCS.](image)

Table 1. Copolymerization conditions of HPDCS.

| Item          | Concentration | DCS   | AM:AA | Initiator | Temperature |
|---------------|---------------|-------|-------|-----------|-------------|
| Content       | 22%           | 0.1%-0.4% | 4: 1  | 0.2%      | 45℃         |

2.3. Structural characterization

The structure of product were characterized by IR and $^1$HNMR. The results (figure 3) were consistent with the proposed structure.

![Figure 3. FTIR spectra of HPDCS and $^1$H-NMR spectra of HPDCS in D$_2$O.](image)

The typical morphologies for HPAM and HPDCS specimens were observed through SEM, which are shown in figure 4. The morphology of HPAM is irregular and rough as a result of the disordered aggregation of polymer chains and the network structure of the linear polymer is dismantled after shearing. In comparison to HPAM, a much smoother surface and the trunk of the network structure for HPDCS could be discovered, implying that the intermolecular entanglement of polyacrylamide chains and hydrogen bonding of D-glucosamine units of HPDCS. The shearing force breaks the branches of HPDCS, but its overall structure is not destroyed. We consider this morphology constructed by the
successfully introduced dendritic chitosan increases the shearing resistance of the hyperbranched polymer.

3. Performance of the branched polymer

3.1. Conventional performance

3.1.1. Thickening performance. From figure 5(a), compared with HPAM, the apparent viscosity of HPDCS solutions were all higher than that of HPAM. The thickening ability of the HPDCS was not much different from that of HPAM at low concentration, while when the concentration was greater than 2000 mg/L, HPDCS has a significantly faster viscosity growth rate than HPAM, which shows that HPDCS has a better thickening performance. In addition, the addition of DCS has a certain effect on the viscosities of copolymer. Because HPDCS has branched polymers, the molecular chains tangle with each other easily and form a certain space mesh structure, which makes the strength of the mesh structure significantly higher than that of HPAM. This structure promotes the thickening performance of the HPDCS to some extent. When the HPDCS solution concentration increases, the distance between the molecular chains will decrease and the interactive force between the chains will increase along with the viscosity of the solution. Thus, the HPDCS shows a stronger thickening performance in relatively high concentrations.

3.1.2. Shearing resistance properties. The effect of mechanical shearing on HPDCS and HPAM were evaluated, and the results are shown in figure 5(b). When the polymer solution was sheared at 3500 rpm for 20 seconds, the highest viscosity retention of HPAM was found to be 91.7%, while that of
HPDCS was 106.3%. Compared with HPAM, the HPDCS has a higher viscosity retention rate under the same concentration: showing a certain shearing resistance ability. The unusual tackifying property was due to the fact that HPAM is a linear structure, mainly in the form of the random molecular lines in the solution, and the molecular chain breaks down along with the viscosity of the solution greatly decreasing in the case of shear. The HPDCS has a special branch structure. The rigidity of the polymer is enhanced greatly due to the support of the branched skeleton. On the one hand, it can improve its shear resistance. On the other hand, the long-chain molecules interaction are related to each other more closely. Therefore, after shearing, the viscosity of polymer solution increases instead of decreasing. Also, the shearing effect on the viscosity of the solution is relatively small due to the rigid glucosamine annular structure in HPDCS. Therefore, the HPDCS has a higher viscosity retention rate compared with the linear HPAM.

Figure 5. (a) Thickening performance; (b) Shearing resistance properties of HPDCS and HPAM and (c) Effect of the α-amylase on the M<sub>n</sub> of the HPDCS and apparent viscosity of the polymer.

3.1.3. Biodegradability experiment. The problems of high viscosity, high emulsification, and difficulty in biodegradation were found in polymer-contained sewage. Treatment by conventional sewage treatment process techniques and agents is unable to meet the requirements of water treatment quality standards. As oil development moves toward low-carbon, environmental protection, the polymer in oil fields needs economy, efficiency, and green eco-friendly performance and biocompatibility. Therefore, it is necessary to study the biodegradability of HPDCS. The influence of enzyme on the molecular weight of HPDCS was studied as shown in figure 5(c). The initial viscometric average molecular weight of the HPDCS was 2.7 million. After the degradation of 45 h by α-amylase, it decreased to 2.12 million. Analyzing figure 5(c), after the degradation of 45 h by α-amylase, the apparent viscosity of HPDCS (treatment) was reduced to 55.2 mPa·s by the initial 81.6 mPa·s. Thus, the viscosity...
retention rate is only 67.7%, and that of HPDCS (blank) is 75.9%. It is shown that the HPDCS exhibits good biodegradable characteristics. For HPAM, the addition of the enzyme has a smaller effect on viscosity. All the experimental results illustrate that the biodegradability of the polymer can be improved to some extent after introducing chitosan into the polymer.

3.2. Sandpacked tube displacement experiment

3.2.1. Injection and mobility control ability. The pressure drop characteristic curves of HPDCS and HPAM under various permeabilities are presented in figure 6(a). A prerequisite of polymer for EOR chemical agent is that the molecular diameter of polymer has good compatibility with formation pore throat. As seen in the figure 6(a), the HPDCS exhibits well injection performance, but it is not as good as HPAM. Since the injection pressure during injection of the polymer solution is increased rapidly, the stable injection pressure of HPDCS was 0.3560 MPa, 0.388 MPa at about 910, and 1040 mD formation, respectively, which is slightly higher than that of HPAM. The pressure is fluctuating at a stable stage of the HPDCS profile. This phenomenon can be explained by the elasticity of hyperbranched polymers. When the polymer enters into the reservoir and the injection pressure reaches a certain value as a result of good deformation characteristics of the polymer branch, the branched chains adsorbed and bridged in the reservoir will break through under the tension of the porous media which promotes the displacement of the deep oil.

The resistance factor RF and the residual resistance factor RRF(calculated by equation (1) and equation (2) [10]) established by HPDCS and HPAM are listed in table 2. At a permeability of 1000mD, the HPDCS solution could reach RF (36.38) and RRF (3.86) while those of the HPAM solution were 27.56 and 3.38 under the same conditions. Also, the figure was less than that in the permeability of 910 mD (39.56 and 4.11). From figure 6(a), the injection pressure of HPAM improved slowly and, a stable pressure was reached at a polymer injection of only 2-4.5 PV. This demonstrated that the time took for the HPAM to adsorb and remain stable was fairly short in the reservoir. In contrast, the HPDCS exhibited good elastic deformation under the tension of the porous media and its injection pressure increased rapidly and eventually reached a higher stable pressure value. And due to its special branched structure, the flexible molecular chains can be deformed through the pore throat of the porous medium, which can avoid serious damage to the molecular chains and the interlocking of the molecular chains more tightly enhances the interaction between the chains, so the HPDCS solution could decrease the water phase permeability remarkably.

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RF = \frac{\lambda_w}{\lambda_p} = \left( \frac{K_w}{\mu_w} \right) / \left( \frac{K_p}{\mu_p} \right) = \frac{\Delta P_w Q_w}{\Delta P_p Q_p} \tag{1}
\]

\[
RRF = \frac{K_{wb}}{K_{wa}} = \frac{\Delta P_{wb} Q_{wb}}{\Delta P_{wa} Q_{wa}} \tag{2}
\]

Table 2. RF, RRF and EOR of HPDCS and HPAM.

| Polymer | Permeability (μm²) | Porosity/% | \(\Delta P_{wa}/MPa\) | \(\Delta P_p/MPa\) | \(\Delta P_{wb}/MPa\) | RF    | RRF   | EOR/% |
|---------|-------------------|------------|------------------------|-------------------|------------------------|-------|-------|-------|
| HPDCS   | 0.91              | 38.39      | 0.0270                 | 0.3560            | 0.0370                 | 39.56 | 4.11  | 21.87 |
|         | 1.04              | 39.21      | 0.0321                 | 0.3880            | 0.0413                 | 36.38 | 3.86  | 24.12 |
| HPAM    | 1.07              | 40.68      | 0.0227                 | 0.2085            | 0.0256                 | 27.56 | 3.38  | 12.74 |
3.2.2. EOR ability. As shown in figure 6(b) and table 2, at the same permeability, the oil recovery remains consistent with the water flooding. After the polymer flooding, the oil recovery obviously increased. Polymer flooding and subsequent water flooding can further increase 24.12% oil recovery compared with 12.74% oil recovery for linear polymer HPAM under similar permeability conditions. The conventional linear polymer HPAM mainly rely on the entanglement between molecular chains to form dynamic retention in the porous medium to achieve mobility control and establish the resistance factor. After the HPAM was sheared, its structure was destroyed and most closely entangled molecular chains were broken resulting in a significant decline in viscosity. The retention of polymer molecules in porous media was greatly reduced causing the mobility control capability of HPAM dropping significantly. Furthermore, the polymer molecules adsorbed on the porous medium were dispersed and caused HPAM to fail to establish a high residual resistance factor after the reservoir was flooded by a large amount of water. Therefore, the ability to reduce the permeability of the water phase was also limited. These were the reasons for the low EOR ability of HPAM. The different from HPAM was that HPDCS rely on its special branch-branched structure to form polymer aggregates by intermolecular interactions to increase the amount of polymer’s mechanical trapping in porous media. In addition, HPDCS formed a network structure in the porous medium and adsorbed on the rock in the form of multi-point adsorption, so it was not easy to be dispersed when the subsequent water injected. The synergy between the above two increase the retention of the polymer in the porous medium which lead to a high residual resistance factor establishment of HPDCS in porous medium. So the HPDCS had more outstanding ability to enhance oil recovery.

4. Conclusions
In this study, a branched polymer based on modified chitosan (HPDCS) for enhanced oil recovery was prepared. Compared with HPAM, HPDCS exhibits better thickening properties and shear resistance. The viscosity retention rate was only 67.7% of the HPDCS after 45 h of biological enzyme action, and it is suggested that the introduction of chitosan can improve the biodegradability of the polymer to a certain extent. We used sandpacked tube displacement experiments to study the ability of HPDCS to establish flow resistance in porous media. Since the HPDCS has a branched structure, it then has a strong shear resistance. After shearing, the mutual entanglement of molecular chains form a network structure that becomes more compact, which can enhance the interaction between the molecular chain, so the HPDCS established a higher seepage resistance and performed excellent mobility control ability. Compared with HPAM, the HPDCS solution of 2000 mg/L showed better oil recovery of 24.12% in the 1.04 μm² porous medium, which demonstrated that the branched polymer has a more outstanding EOR ability than that of the linear polymer HPAM under the same conditions.
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