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Amphiphilically modified chitosan copolymer for enhanced oil recovery in harsh reservoir condition

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ABSTRACT

A novel amphiphilically grafting natural chitosan copolymer (PAMCS) was prepared by using one step water-free radical polymerization strategy and the basic parameters for PAMCS were systematically characterized. The rigid D-glucosamine unit, intermolecular association and hydrogen bonding synergistically endowed PAMCS solution with rheological properties, super-high salt resistance and temperature tolerance in harsh reservoir condition. PAMCS solution exhibited viscoelastic behavior and formulated the unique displacement mechanism in comparison to that for partially hydrolyzed polyacrylamide. Moreover, the mass concentration, injective rate and polymer solution slug related to oil recovery efficiency for PAMCS were investigated from the economic point.

Introduction

Almost 70% crude oil of the Original Oil in Place (OOIP) is left in the subterranean formation after water flooding because of the unfavorable water/oil ratio resulting in the severe water breakthrough and the rapid increase of water cut [1,2]. It is the target of chemical flooding for enhanced oil recovery (EOR). Partially hydrolyzed polyacrylamide (HPAM) has been widely used as a water-soluble polymer in chemical EOR process due to its favorable solubility and the capability of adjusting displacing fluid mobility in the mild reservoir condition [3]. With the developments exploring to deeper, and the harsh reservoirs, HPAM faces with considerable challenges. The linear flexible chains deform extremely at upgraded temperature, and the negative charges carried by carboxyl groups are forced by cationic ions in high salinity condition, resulting in the fragile thickening efficiency for HPAM [4–6]. Furthermore, the mechanical shear stress is accompanied with the lifetime of polymer solution from the injectors to the produces, which is associated with the irreversible shear degradation and impairs its viscosifying power.

Many researchers proposed that hydrophobically associative polymers where HPAM is modified with a small proportion of hydrophobic moieties, can somewhat improve its linear flexible chains [7–10]. Above the critical associative concentration (CAC), hydrophobic groups interact between polymer chains to form a transient network resulting in the desirable rheology modifiers with versatile of applications. Controlling the hydrophobic intermolecular association to manipulate the strength of topological structure could guarantee polymer solution benign stability in harsh condition [11,12]. Owing to the particular shearing thinning and thixotropic properties, and high interfacial activities because of the presence of hydrophobic groups [13], the potential of those polymers in EOR applications has been of great interest in petroleum industry.

Given the plunging crude oil price worldwide, the strategy to manipulate chemical flooding system at lower cost with higher oil recovery efficiency has attracted intense attention. Considerable interest has been generated in modulating smart polymers based on availably natural polymers, such as polysaccharides [14–18]. Chitosan is formed by extensive deacetylation of chitin that is a typical polysaccharide outranked only by cellulose [19], comprising

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a large proportion of D-glucosamine units as well as a small proportion of N-acetyl-glucosamine units. It is renewable and eco-friendly that has been extensively investigated for macroscopic materials [20], nanocarriers [21], genetic engineering [22] and biomedical areas [23]. With the versatile number of structures and possible configurations, the general modification notion covered reactions with hydrophilic groups to increase water solubility and with hydrophobic groups to facilitate the self-assembly into the intelligent structures of modified copolymer [19,24–26]. Moreover, the D-glucosamine unit of chitosan is a rigid structure of six member heterocyclic ring [27], which might provide robust steric effect to resist high temperature degradation. However, the reports on synthesis of amphiphilically modified chitosan that are used as a chemical flooding agent for EOR are rare.

According to Mandal et al. [28,29], significant works remain indispensable for economic implementation of chemical EOR process due to the fact that the composition of crude and reservoir geological conditions vary from field to field, and the effect flooding agent on the crude oil and rock matrix is naturally complex. Thus, in this work, hydrophilic monomers and hydrophobic monomer surface grafting modified chitosan, namely PAMCS was prepared (Fig. 1a) by a simple water-free radical polymerization technique. IR, ^{1}H NMR spectra and SEM experiment have been done to characterize the structure of PAMCS. We have investigated the comprehensive properties for PAMCS solution, such as viscosified power, rheological performance, salt resistance, temperature tolerance and long-term stability in harsh condition. Moreover, a series of displacement experiments were carried out to investigate the oil recovery potential for PAMCS.

Experimental

Materials

Chitosan (AR) purchased from Alfa Aesar (UA), the degree of deacetylation was 85.6%, and the weight-average molecular weight (M_w) was 2.5×10^4 g/mol. Acrylamide (AM, CP) and acrylic acid (AA, AR) were purchased from Chengdu KeLong Chemical Reagent Co. Ltd., (China). AM was used after purification and AA was used without further purification. 2, 2′-azobis (2-amidinopropane) dihydrochloride (AIBA, 99.99%) purchased from Alfa Aesar was used as received. 2-acrylamido-dodecyl sulfonate ($AMC_{12}S$) was prepared in the laboratory according to the literature [30]. HPAM, one of the most widely used polymers that employed in oilfields for oil recovery, was purchased from SNF Floerger Group (France), trade name AN926: M_w 8.3×10^6 g/mol, hydrolysis degree 23.6%. Its structure was listed in Fig. 1c. Crude oil and formation water were obtained from a certain block in Dagang Oilfield (China). Sandstone cores used for core flooding test were outcrop cores, which shared similar geologic features as the selected block as they are at the same tectonic level. The formation averaged temperature is 90 °C and averaged total salinity 20,813 mg/L with the averaged water permeability (K_w) of 100 mD. The formation water was filtered twice to remove undissolved particles and the composition of the formation water is listed in Table 1. The viscosity and density of crude oil are 8.7 mPa s and 0.88 g/cm^3 at the reservoir condition. The SARA fractions of crude oil are as follows: saturated hydrocarbon 51.21%, aromatic hydrocarbon 19.07%, resin 29.46% and asphaltene 0.26%. The paraffin content is 18.15%. All supplementary materials

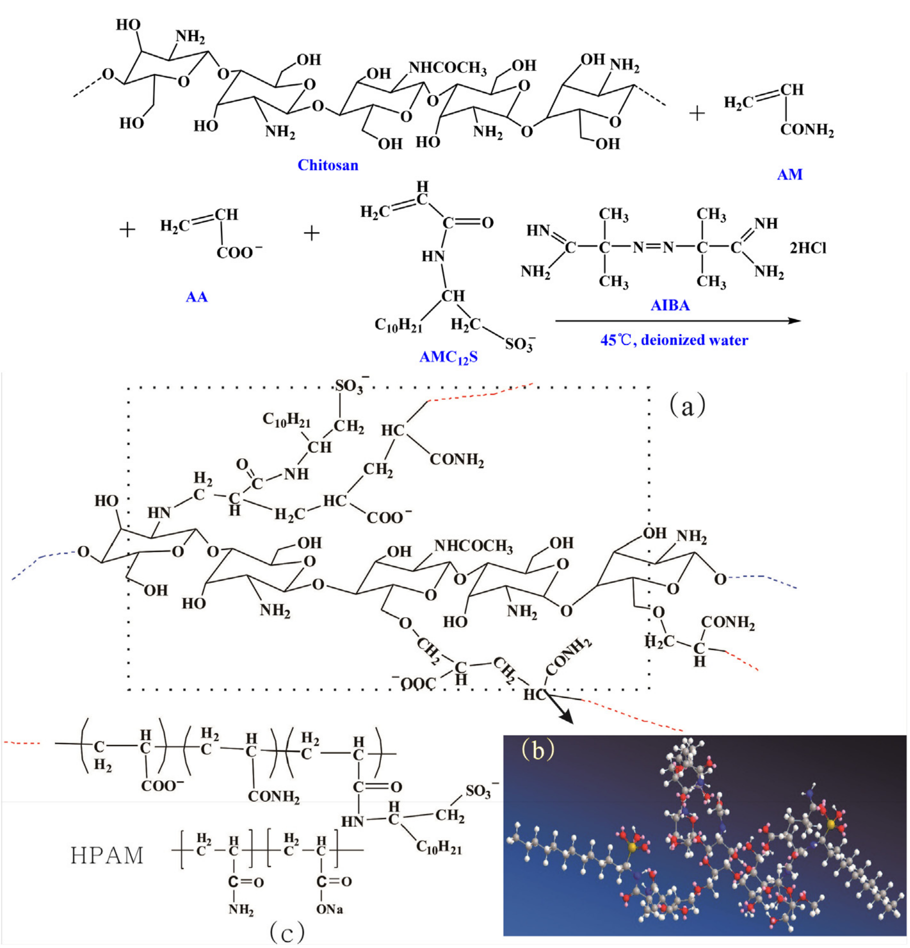

Fig. 1. Schematic representation of the surfactant free synthesis of (a) amphiphilically modified chitosan (PAMCS), (b) the 3D structure of one fragment of PAMCS and (c) the structure of HPAM.