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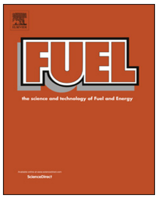

Full Length Article

pH-switchable and CO_2-switchable viscoelastic fluids based on a pseudo-hydrophobically associating water-soluble polymer

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ABSTRACT

The non-hydrophobically associating water-soluble polymer (DPAM) of acrylamide (AM) and dimethylamino propyl methacrylamide (DMAPMA) was synthesized. Then pH-switchable and CO_2-switchable viscoelastic liquids based on DPAM and anionic surfactant sodium dodecyl sulfate (SDS)(referred to as DPAM-SDS) were developed. When minor HCl aqueous solution was added into the DPAM and SDS aqueous mixture or CO_2 was bubbled into it, the tertiary amine groups of DPAM were protonated to form quaternary ammonium groups, some of which in the same quaternary ammonium groups of DPAM "bridged" some SDS through noncovalent electrostatic attraction, behaving like a pseudo-hydrophobically associating water-soluble polymer and forming viscoelastic fluids as checked through environmental scanning electron microscope(ESEM) and rheology. Upon removing of CO_2 or back of pH by minor NaOH aqueous solution, the quaternary ammonium species of DPAM were deprotonated back to tertiary amine groups, separating the pseudo-hydrophobically associating water-soluble polymer back to DPAM and SDS molecules, which resulted in forming low-viscosity water solution. The switchable viscoelastic conversion can be repeated.

1. Introduction

Viscoelastic fluids based on hydrophobically associating water-soluble polymers (HAWPs) have become the focus of research in the past prevailingly by reason of a small number of hydrophobic groups and rheological properties [1–9]. The HAWPs can form 3D-network structures by the hydrophobic association to reveal significant macroscopic viscoelastic properties, which are drawing more and more attention in academia and industry [10–19].

However, HAWPs such as common copolymers of acrylamide and N-benzylacrylamide and copolymers of acrylamide and octadecyl methacrylate still have the disadvantage of poor solubility because of their special hydrophobic monomers. Meanwhile, the common method for the synthesis of HAWPs is to add surfactants to the reaction system to emulsify and solubilize the hydrophobic monomers [20–21]. However, it is difficult to remove surfactants after reaction [22] and can bring about the chain transfer problem in the polymerization process.

Yujun Feng [23] research group developed a new type of pH-switchable wormlike micelles through mixing N-erucamidopropyl-N,N-dimethylamine and maleic acid. The viscosity of the mixture was reversible by regulating the pH, possessing the advantages of a simple and easy process and recyclable materials. After that their research group [24] also designed CO_2-switchable viscoelastic fluids based on sodium dodecyl sulfate (SDS) and N,N,N′,N′-tetramethyl-1,3-propanediamine (TMPDA). This system could be reversibly varied between high-viscosity and low-viscosity fluids by bubbling and removing CO_2 in turn.

Inspired by such a pseudo-gemini concept, in place of synthesizing HAWPs directly, we developed a viscoelastic fluids including commercial surfactant sodium dodecyl sulfate SDS and a non-hydrophobically associating water-soluble polymer DPAM that was easy to synthesize, which can transform a pseudo-hydrophobically associating water-soluble polymer by regulating pH to acidity or bubbling CO_2. The structure of the synthetic DPAM was checked through the IR and ^{1}H NMR spectra. The DPAM-SDS solution could be convertibly varied between high-viscosity and low-viscosity fluids by alternately adjusting pH by minor NaOH and HCl aqueous solution or bubbling and removing CO_2. Through this research, we could provide a new idea for construction of viscoelastic fluids based on pseudo-hydrophobically associating water-soluble polymers.

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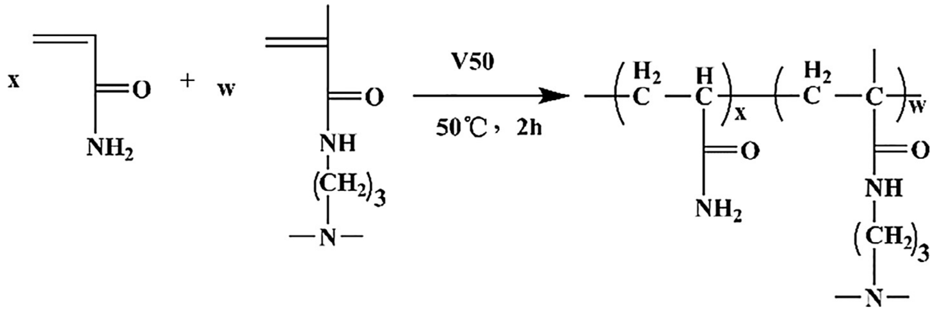

Scheme 1. Synthesis route of DPAM.

2. Materials and methods

2.1. Materials

Acrylamide (AM, AR), ethanol (> 99.7%), sodium dodecyl sulfate (SDS, AR) and dodecyl trimethyl ammonium bromide(DTAB) were purchased from Chengdu Kelong Chemical Factory. 2, 2′-azobis (2-methylpropiona- midine) dihydrochloride (V50, 97%) was purchased from Aladdin chemicals. Dimethylamino propyl methacrylamide (DMAPMA) was purchased from Shanghai Mackin Biochemical Co., Ltd.

2.2. Synthesis of DPAM

The synthesis route of DPAM was showed in Scheme 1. The reaction was carried out in a 150 mL three-necked flask. The reactants including 189.9 mmol of AM and 9.9 mmol of DMAPMA were dissolved in 86.13 g deionized water. The reactor was put into a water bath under a stream of carbon dioxide at 25 °C for 30 min. V50 as initiator was added. The reactor was carried out at 50 °C for 2 h, and then a gel-like copolymer was precipitated with ethanol and dried in a vacuum drying oven to evaporate water and ethanol.

2.3. Sample preparation

The sample preparation method was described through taking DPAM-SDS solution as an example. The sample solution was prepared through dissolving a certain amount of DPAM and SDS in deionized water, and we can obtain 0.5 wt%DPAM-0.015 wt% SDS solution and 0.5 wt%DPAM-0.025 wt% SDS solution. Minor HCl aqueous solution was added to the DPAM-SDS solution to get DPAM-SDS-HCl solution. CO_2 was bubbled into DPAM-SDS solution at room temperature with a fixed flow rate of 0.06 $L\cdot min^{-1}$ for 10 min to get DPAM-SDS-CO_2 solution. Minor NaOH aqueous solution was added to DPAM-SDS-HCl solution to regulate pH back to initial state and N_2 was bubbled into the DPAM-SDS-CO_2 solution at 70 °C at the same flow rate to remove CO_2 efficiently. Other sample solutions including the DPAM solution, SDS solution, DTAB solution and DPAM-DTAB solution were prepared in the same way as the DPAM-SDS solution.

2.4. Characterization and measurements

2.4.1. Spectroscopic characterization

FT-IR spectrum of DPAM was recorded on a Nicolet Nexus 170SX Fourier transform infrared spectrophotometer through KBr disks in a range of 4000–500 cm^{-1}. ^1H NMR spectrum of DPAM in D_2O was performed on a Bruker ASCENT-400 NMR.

2.4.2. Rheology measurements

The correlation between apparent viscosity of the prepared sample solutions and pH was investigated by NDJ-8S under conditions of the No. 2 rotor and the fixed rotate speed of 6 $r\cdot min^{-1}$ at 25 °C. The viscoelasticity and anti-shear ability were measured at 25 °C by HAAK MARSIII Rheometer.

2.4.3. Environmental scanning electron micrographs measurements

Microstructure of prepared sample solutions could be observed through Phenom Pro scanning electron microscopy. The samples were prepared by the vacuum sublimation freezing–drying technique.

3. Results and discussion

3.1. Characterization of DPAM

3.1.1. The FT-IR spectrum of DPAM

The FT-IR spectrum of DPAM was shown in Fig. 1. From Fig. 1, characteristic absorption bands at 3176 and 1689 cm^{-1} are assigned to N—H and C═O stretching vibrations of amide groups of AM. The peaks at 2931 and 2807 cm^{-1} are ascribed to the C—H stretching vibrations of —CH_2— and —CH_3 groups in DPAM. The characteristic peaks of N-(CH_3) at 1411 cm^{-1} and —NH—CH_2— at 1315 cm^{-1} confirm the existence of DMAPMA. The above analysis results demonstrate preliminarily that the non-hydrophobically associating water-soluble polymer (DPAM) has been synthesized successfully.

3.1.2. The ^1H NMR spectrum of DPAM

To further demonstrate the structure of DPAM, the ^1H NMR spectrum of DPAM was shown in Fig. 2. The chemical shift peaks of —CH_2—, —CH—CO— and NH_2–in polyacrylamide appear at 1.68, 2.25 and 6.90 ppm, respectively. —CH_2— and —CH_3 bonded with N atom of tertiary amine of DMAPMA are observed at 2.41 and 2.14 ppm. The peak at 7.68 ppm (marked as 6) is due to the protons of secondary amine of DMAPMA. The peaks at 1.86 and 1.25 ppm are for —CH_2— and —CH_3 of DMAPMA. Thus, the ^1H NMR spectrum shows that the polymer is a

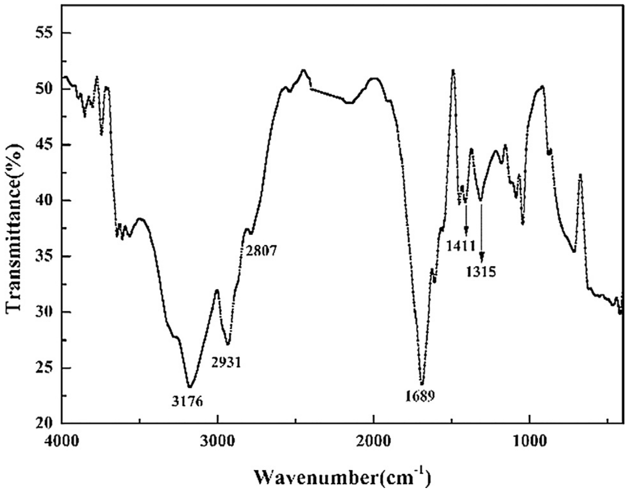

Fig. 1. The FT-IR spectrum of DPAM.