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Synthesis and aggregates of cellulose-based hydrophobically associating polymer

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Abstract

A novel cellulose-based hydrophobically associating water-soluble polymer-cellulose octaonate sulfate (COS) was synthesized in this paper. The basic physico-chemical properties such as surface tension and the critical aggregation concentration (*cac*) were measured by the conventional Wilhelmy plate method. The obtained *cac* value was compared with environmental scanning electron microscopy (ESEM) and Rheology data. All these results indicated that *cac* of this amphiphilic polymer was between the range 0.04 and 0.2 wt% and the corresponding surface tension was around 55 mN/m. The conformation of aggregates and size of particles in aqueous solution were carefully investigated by ESEM and dynamic laser scattering (DLS) measurements. When the concentration is around 0.04 wt%, loose aggregates are formed; around 0.5 wt%, network structure formed. DLS results indicated that average size of particle was increased from 54.7 nm to 73 nm and *finally to 168.1 nm* with the increase of concentration from 0.04% to 0.1% and *even to 0.2%*. These results suggested that almost all of micelles in aqueous solution aggregated at the experimental concentration range 0.04–0.5 wt%. Rheological properties of this polymer were similar to hydrophobically associating polymers' (HMP). As the shear rate increased, the solution passed through a shear-thickening region before exhibiting a sharp decrease in viscosity, eventually exhibited Newtonian behavior.

Keywords: Cellulose; Cellulose octaonate sulfate (COS); Micelles; Aggregation; Critical aggregation concentration

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1. Introduction

Amphiphilic polysaccharide-based polymers have been extensively studied not only because of scarcity of petroleum resource, but also a positive alternative to exiting non-biodegradable polymers (Arvanitoyannis, 1999; Psomiadou, Arvanitoyannis, & Yamamoto, 1996). Now, they have attracted growing attention for their wide range of applications in surfactant industry, latex paint technology, oil recovery, cosmetics, liquid crystal and medicine. Cellulose-based associating polymers are one of the most extensively studied directions during the last decades.

Landoll (Landoll, 1982) was the first to develop cellulose as hydrophobically associating water-soluble polymers. In his work, nonionic cellulose ethers such as hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC) and methylcellulose (MC), was employed as raw materials for hydrophobization by reaction with long-chain *n*-alkyl epoxides. This new class polymer had unique solution properties due to interchain association. Following his research, a substantial body of literature dealing with this new type of cellulose-based polymers has been developed (Aubry & Moan, 1994; Gelman & Barth, 1986; Rosilio, Albrecht, Baszkin, & Merle, 2000; Sau & Landoll, 1989; Srokova, Tomanova, Ebringerova, Malovikova, & Heinze, 2004; Tanaka, Meadows, & Phillips, 1990; Srokova, Talaba, Hodul, & Balazova, 1998). However, almost in all cases, they are water-soluble cellulose derivatives (such as carboxymethyl cellulose, sulfoethyl cellulose, cellulose sulfate, et al.) substituted with hydrophobic side groups such as alkyl halides, acid halides, acid anhydrides, isocyanates or epoxides. The introduction of bulky hydrophobic substituents to water-soluble

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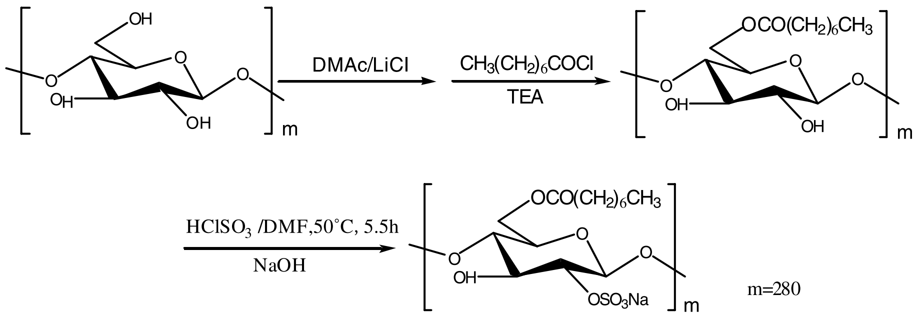

Scheme 1. Synthetic route of cellulose derivative.

cellulose derivatives has been achieved under heterogeneous conditions; the degree of substitution (DS) was limited and regional variation in the degree of crystallinity/amorphous of the polymer resulted. This gives rise to the diversifications in the hydrophobic/hydrophilic nature of the polymer backbone.

These so-called hydrophobically associating water-soluble polymers have a strong tendency for intra- or intermolecular hydrophobic self-association and interaction with surfactants. Most of the literatures made on deals with the rheological properties and association between polymers and surfactants added (Dualeh & Steiner, 1990, 1991; Goldszal, Costeux, & Djabourov, 1996; Kastner, Hoffmann, Donges, & Ehrler, 1994, 1996; Lliopoulos & Olsson, 1994; Loyen, Lliopoulos, Audebert, & Olsson, 1995; Steiner, 1991; Tanaka, Meadows, Willians, & Phillips, 1992; Thuresson, Nilsson, & Lindman, 1996; Thuresson, Nyström, Wang, & Lindman, 1995; Thuresson, Söderman, Hansson, & Wang, 1996; Varelas & Steiner, 1992; Varelas, Dualeh, & Steiner, 1994; Zhao, Khin, Chen, & Chen, 2005). These studies are important both from the numerous uses in a wide of industrial fields and a fundamental point of view for structure and the mechanism operating in the polymer-surfactant association. However, the detailed microstructure of micelle-like clusters is not yet well established.

In this paper, a novel synthetic route for amphiphilic cellulose derivatives was reported. The new pathway is depicted in Scheme 1. Different from literature's synthetic route, our procedure is as following: hydrophobic side chain is introduced in backbone of cellulose, then hydrophilic groups. Hydrophobically cellulose derivative-cellulose octaonate can be easily synthesized by the reaction between cellulose with Octanoyl chloride in homogeneous LiCl/DMAc solution, the degree of substitution (DS) was easily controlled. Furthermore, this hydrophobically cellulose easily swells even to dissolve in DMF, amphiphilic cellulose-based polymers could be easily obtained by sulfating reaction with chlorsulfonic acid in DMF medium.

Additionally, the basic physico-chemical properties such as surface tension and *cac* were investigated by the Wilhelmy plate method to compare with the results obtained by micelles aggregating (Nishikawa, Yekta, Pham, & Winnik, 1998). To facilitate a straightforward understanding of the association, the aggregates microstructure at a wide range of concentration and size of particle in aqueous solution were investigated by ESEM and DLS altogether with rheology, which have not yet been reported for hydrophobically associating water-soluble cellulose derivatives. In our future research, the effects of hydrophobic chains' length and the differences of hydrophilic groups on the properties of this family cellulose derivative will be investigated for potential industry applications.

2. Experimental

2.1. Materials and reagents

Avicell PH-101 (Microcrystalline cellulose, degree of polymerization = 280) was purchased from Changshu Medial Supplements Co., Ltd. Jiangshu Province, P.R. China. Cellulose sulfate in this study was prepared according to the literature (Schweiger, 1979). Dimethyl acetoamide (DMAc), lithium chloride (LiCl), dimethyl formamide (DMF), triethylamine (TEA), pyridine were dried and purified before use. Octanoyl chloride, methanol and chlorsulfanic acid were reagent grade and used without further purification.

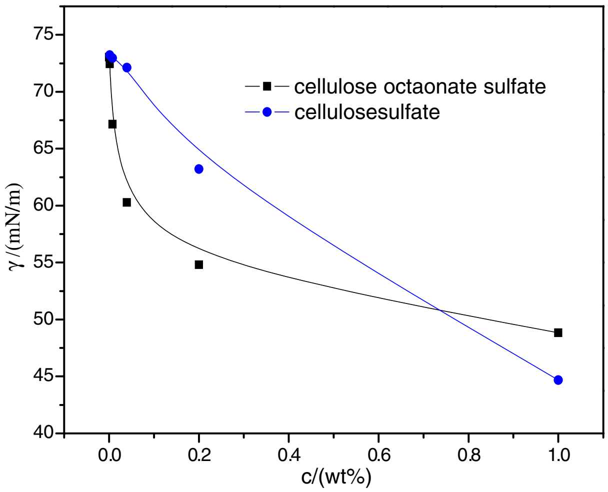

Fig. 1. Surface tension–concentration curve of cellulose sulfate and cellulose octaonate sulfate.

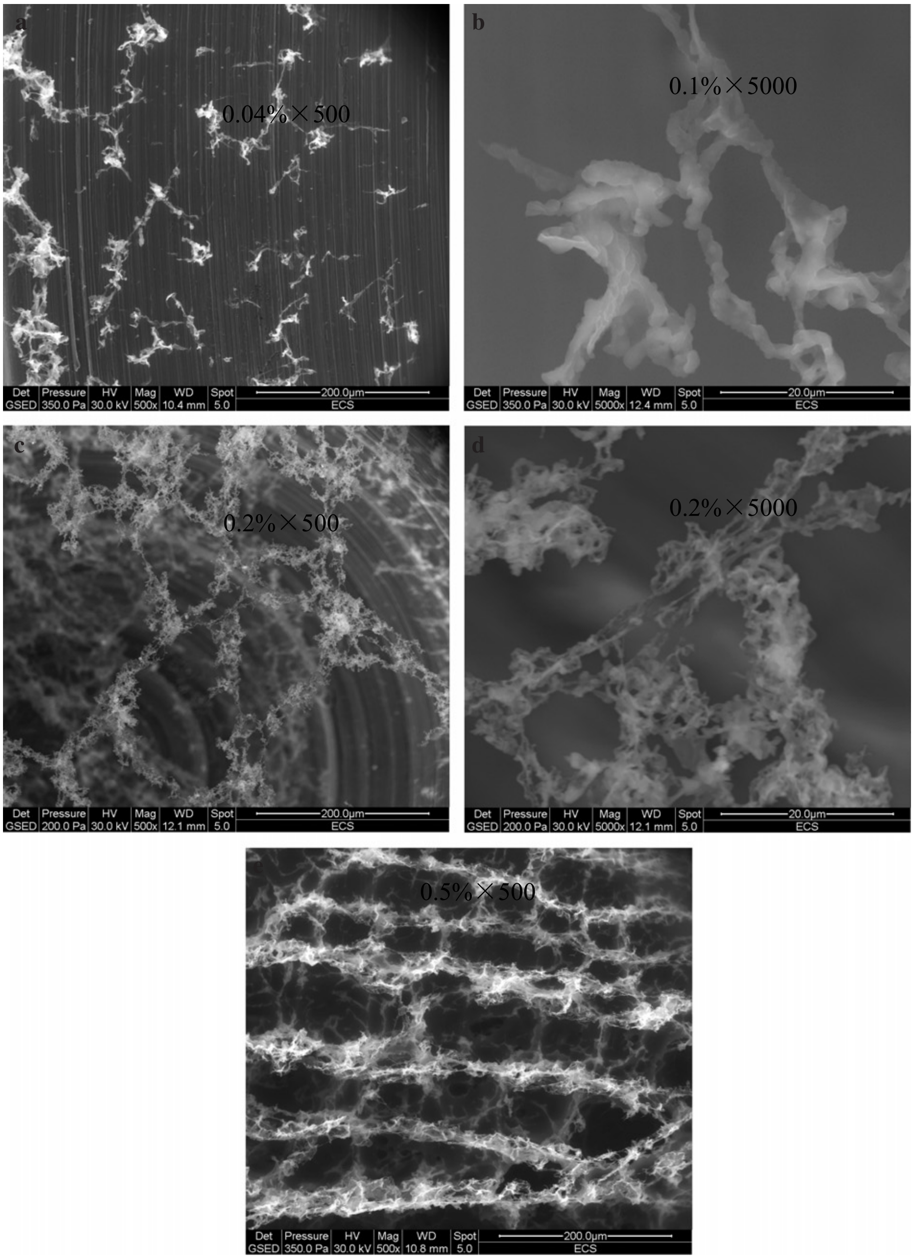

Fig. 2. ESEM of COS in aqueous solution with different concentrations.

2.2. Synthesis of cellulose octaonate (CO)

The solution of (2.5 wt%) of cellulose in DMAc/LiCl was accomplished by a known procedure (McCormick and Dawsey, 1990). The synthetic pathway of cellulose octaonate was slightly modified according to the previous literature (Callais & McCormick, 1987). Briefly, to the above cellulose solution, 6.52 mL (0.047 mol) TEA in 12.5 mL DMAc was added slowly in one portion, then a solution of 8.02 mL (0.047 mol) octanoyl chloride in 25 mL DMAc was added dropwise over a period of 1 h, and the resultant mixture was stirred for 24 h at room temperature. The product was isolated as white powers by precipitation from large volume water, purified by soxhlet extraction with methanol for 48 h, and vacuum dried at 50 °C for 48 h. Elemental analysis: C, 52.32; H, 8.53 (calcd. DS = 0.43). I.R.: ester C═O, 1750 cm^{-1}; methyl C—H, 2960 cm^{-1}; methylene C—H, 2920 cm^{-1}. CP/MAS ^{13}C NMR: C═O, 171 ppm.

2.3. Synthesis of cellulose octaonate sulfate (COS)

Cellulose octaonate (1.5 g) above was suspended in DMF (30 mL), and magnetically stirred overnight. Chlorsulfanic acid 10 mL (0.1504 mol) was added dropwise into stirred DMF 20 mL (0.2596 mol) at 0 °C under N_2 atmosphere. After completely dripped, the solution was kept in agitation for 1 h, and then the suspension of CO and DMF was added to the above solution. The mixture was heated to 50 °C and stirred at this temperature for 5.5 h under N_2 atmosphere. The reaction solution was neutralized with

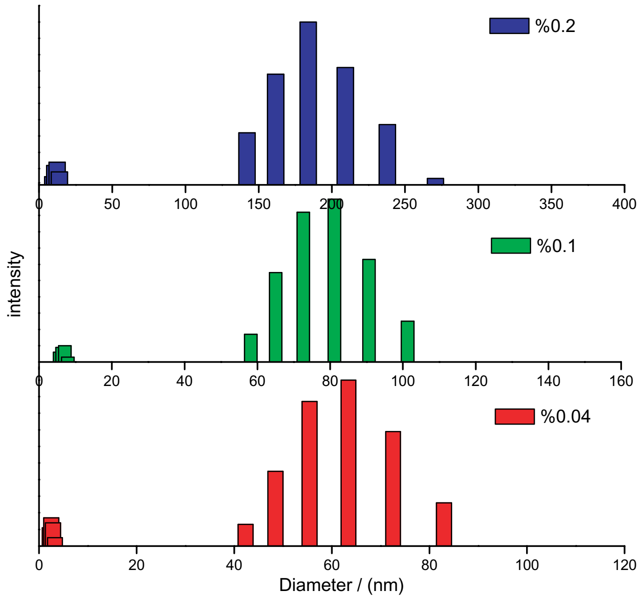

Fig. 3. The hydrodynamic diameter distribution of COS with different concentration.

20% NaOH to pH 7 in ice-water bath, and the filtered solution was dialyzed (MWCO 8000) against distilled water, then lyophilized and cellulose octaonate sulfate (COS) powder was obtained. ICP analysis: S, 6.3 (calcd. $DS_{SO4} = 0.53$). I.R.: C—O—S, 803 cm^{-1}; S=O, 1261 cm^{-1}; ester C=O, 1750 cm^{-1}; methyl C—H, 2958 cm^{-1}; methylene C—H, 2858 cm^{-1}. ^{13}C NMR: C=O, 174.22 ppm; $-(CH_2)_6CH_3$, 13.63–38.33 ppm; C-1, AGU, 101.62 ppm; C-6 and C-6s, AGU, 62.64 ppm and 65.57 ppm; C-2, AGU, 72.74 ppm. The total synthesis pathway was presented in Scheme 1.

2.4. Characterization

^{13}C NMR spectra was recorded at 400 MHz on a Varian Unity-Plus 400 spectrometer (25 °C in D_2O). The FT-IR spectra were recorded on a BIO-BAD EXALIBUR FTS-3000 Fourier transform spectrometer using the KBr pellet method. The surface tension was measured by the Wilhelmy plate method with Dynamic Contact Angle Analyzer (Germany) at 25 °C. ESEM images of micelles conformation were observed directly with Environmental scanning electron microscope (Quanta 200, FEI, USA). The aqueous solution was quenched at −10 to −20 °C, water in solution sublimed gradually under vacuum, then the naked micelles particle were observed. The dynamic light scattering (DLS) experiments were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 514 nm. All samples were prepared by filtering about 1 mL of the micellar complexes solution with a 0.80 μm Millipore filter into a clean scintillation vial and then measured at 25 °C. The polymer solution viscosity was measured using a Stress Tech ETC2 rheometer with a DC50 temperature control (water circulating bath).

3. Results and discussion

3.1. Critical aggregation concentration and surface tension

Fig. 1 showed the relationship between surface tension and concentration of cellulose sulfate and cellulose octaonate sulfate. The *cac* was obtained from the breakpoint of the curve of surface tension versus concentration. Surface tension at *cac* (γ_{cac}) was also determined from the curve. As shown in Fig. 1, the breakpoint was not detected for single cellulose sulfate, while obvious breakpoint was obtained for cellulose octaonate sulfate. The *cac* of cellulose octaonate sulfate was around 0.04–0.2 wt% and corresponding surface tension was 55 mN/m. This indicated that the capacity for reducing surface tension of cellulose octaonate sulfate was significantly enhanced in comparison with single cellulose sulfate. As shown in Fig. 1, the surface tension drops greatly as the concentration of COS increases up to the *cac*.

3.2. Micelles conformation in aqueous solution

Fig. 2 shows the ESEM of COS in aqueous solution with various concentrations. From Fig. 2, almost no aggregate was observed below the concentration of 0.04 wt%. Under experimental conditions, a concentration at 0.008 wt% was employed and no micelle-like aggregates were observed. However, when the concentration was above 0.04 wt%, there were more micelle-like clusters. These aggregates are due to the hydrophobic interactions of the hydrophobically modified groups; the critical concentration for micelle-like clusters could be identified as around 0.04 wt%. This value is close to that of the Wilhelmy plate method.

As presented in Fig. 2, the micelles gradually associated with the increasing of concentration. When the concentration is around 0.04 wt%, loose aggregates consisted of a few chains, are formed because of hydrophobe linking; this phenomenon is slightly similar to the flower micelles of a telechelic hydrophobically modified polymers (HMP). At the concentration of 0.5 wt%, the aggregates start to associate together to form a gel (compact network), analogous to loop-to-bridge transition of a telechelic HMP (Nishikawa et al., 1998).

3.3. Particle distribution of cellulose-based associating polymer in aqueous solution

In Fig. 3 the distribution of hydrodynamic diameters obtained by DLS as function of concentration are presented. As shown in Fig. 3, with the increase of polymer concentration from 0.04% to 0.1% even to 0.2%, average size of article was increased from 54.7 nm to 73 nm, finally to 168.1 nm. This may be assigned to the interaction between the hydrophobic moieties of different polymer chains that results in the formation of loose and compact aggregates. This result corroborates the interpretation given for the ESEM data.

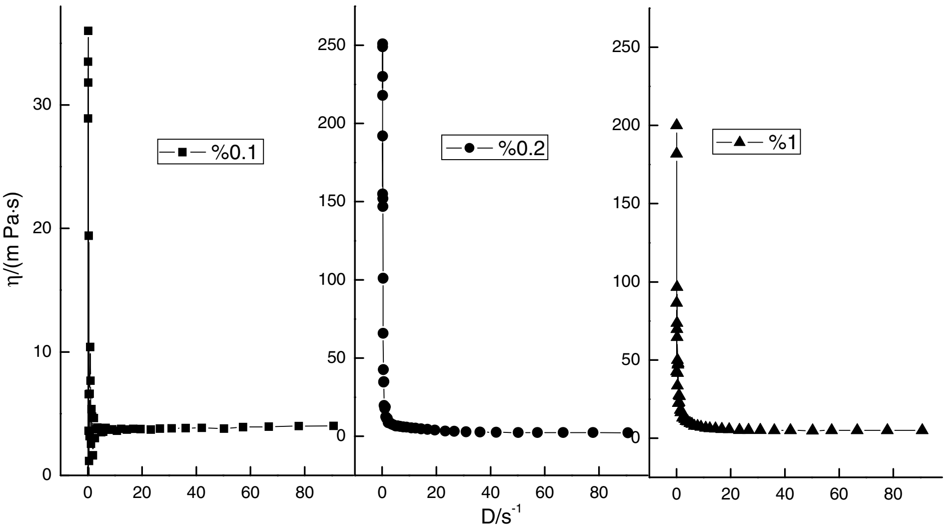

Fig. 4. Viscosity of COS solutions as a function of shear rate.

3.4. Rheological properties

Fig. 4 plots the apparent viscosity of COS solution against shear rate at various concentrations. In Fig. 4, rheological properties of cellulose-based amphiphilic polymer were almost similar to HMP (Maestro, Gonzalez, & Gutierrez, 2002) in the investigated concentration range. With shear rate increased, viscosity rapidly decreased; the shear rate kept increasing, the tendency of decreasing decelerated, eventually apparent viscosity remained approximately constant. This phenomenon is attributed to the shear enhanced interchain association of hydrophobes as the imposed flow elongates and aligns the polymers to promote the intermolecular bridging via the hydrophobic interaction. However, in a stronger flow, the links can be disrupted, thus the solution becomes shear thinned. At the concentration of 0.2 wt%, the dramatically high viscosity value of 250 mPa · s was attained because of the formation of a gel-like structure arising from the dominant intermolecular association. Regions of both shear thinning and shear thickening behavior have been observed at this concentration. This concentration c* was marked as *cac*, which is in the range of concentration obtained above. At concentrations above c*, intermolecular hydrophobic associations between polymers dominate polymer behavior. At concentrations below c*, intramolecular hydrophobic associations dominate.

4. Conclusions

A novel synthetic route of amphiphilic cellulose derivative-cellulose octaonate sulfate (COS) was developed in this paper. The basic physico-chemical properties such as surface tension and *cac* were studied by the conventional Wilhelmy plate method. And the *cac* value obtained was compared with ESEM and rheology data. Results indicate that the critical aggregate concentration was almost in the range of 0.04–0.2 wt% and the corresponding surface tension was around 55 mN/m.

ESEM and DLS data show that the micelles in aqueous solution almost aggregate at the experimental concentrations and the formation of network structure arise from the dominant intermolecular association at 0.5 wt%. Rheological properties of this polymer were similar to hydrophobically associating polymers' (HMP). As the shear rate increased, the solution passes through a shear-thickening region before a sharp decrease in viscosity, and eventually Newtonian behavior.

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