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Amphiphilic cellulose: Surface activity and aqueous self-assembly into nano-sized polymeric micelles

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Abstract

The aim of the present study was to design amphiphilic cellulose that can self-assemble into polymeric vesicle or as non-toxic surfactants. Sulfate was firstly introduced as hydrophilic groups, then the hydrophobic groups for three cellulose derivatives. Effects of the hydrophobic length on the surface tension and critical aggregate concentration (cac) were investigated by the conventional Wilhelmy plate method. Results showed that the cac value decreased from 0.28 to 0.08 wt% and the corresponding surface tension increased from 44 to 55 mN/m when the hydrophobic chain length changed from C_8 to C_{18}. The aqueous self-assembly of the modified polymer was investigated using transmission electron microscopy (TEM) and dynamic laser scattering (DLS). Results showed that three cellulose derivatives were capable of forming polymeric micelles in water with an average particle diameter ranging from 20 to 67 nm. And the diameter of the nano-micelles was proportional to the length of hydrophobic chain under the experimental conditions. These amphiphilic polymers showed more remarkable shear shinning rheological behavior as expected since higher shear rates lead to disruptions of hydrophobic associations. These data suggest that the amphiphilic cellulose derivative may form nano-micelles and might find use as surfactant or a potential drug carrier.
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1. Introduction

In recent years, there has been an increasing trend in society toward more efficient utilization of agro-industrial residues for the production of various products. Cellulose is the most abundant naturally occurring organic molecule on the planet and a potentially limitless source of energy. It was estimated that 10^{11}–10^{12} tons are synthesized annually by photosynthesis of plants. However, the utilization of inedible cellulose as a chemical feedstock has been limited because cellulose is very stable chemically and extremely insoluble due to its robust crystal structure. For many centuries it has served mankind as a construction material, mainly in the form of intact wood and textile fibers such as cotton of flax, or in the form of paper and board. Though the application of cellulose as a precursor for

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chemical conversions was exploited extensively even before its polymeric nature was determined and well understood. Recently, cellulose-based polymer have attracted more considerable attention for its favorable characteristics including biotolerability, biodegradability, protein rejecting ability, and so on. The absence of abundant functional groups provides opportunities for modification or functionalization. Cellulose and their water-soluble derivatives can be tailed to have desired properties after appropriate chemical modifications. The amphiphilic nature gives them a wide and interesting application spectrum, for instance as rheology modifiers, emulsion stabilizer, surfactants, surface modifiers for liposomes and nanoparticles, and as drug delivery vehicles.

Since the pioneering work of Landoll [1], polymeric surfactants prepared by hydrophobic modification of hydroxyethyl cellulose (HEC) have been widely studied. Their solution properties have been extensively detailed through the concept of associative behavior. Now there has developed a substantial body of literature dealing with this new type of amphiphilic polymers [2–7]. In most cases, they are water-soluble cellulose derivatives (carboxymethyl cellulose, 2-sulfoethyl cellulose, cellulose sulfate, etc.) substituted hydroxy with hydrophobic side groups (long-chain alkyl or acyl halides, long-chain alkyl epoxy compounds, etc.). Besides, amidation of carboxyl group of carboxymethyl cellulose by alkylamines also yields water-soluble associative polymers exhibiting tensioactive properties [8–11]. Introduction of bulky hydrophobic substituents to water-soluble cellulose derivatives has usually been performed under heterogeneous conditions; the degree of substitution (DS) was very limited. In view

of this, another synthetic route has been reported in our previous literature [12]. Firstly, hydrophobic groups were introduced to cellulose backbone in LiCl/DMAc solution, and then hydrophilic groups. Cellulose octaonate sulfate (C-8) was successfully synthesized and DS was easily controlled.

It was reported earlier that hydrophobic moieties of amphiphilic polysaccharide polymers were able to self-aggregate as nanoparticles through hydrophobic interactions when above a certain concentration in aqueous solution [13–16]. Aqueous solutions of hydrophobically modified polysaccharide derivatives have been investigated with respect to their viscoelastic properties, aggregation numbers, and surface tensions. Several previous reports have described the interactions between hydrophobically modified water-soluble polymers and anionic surfactants, and have discussed the unique rheological properties of these mixed polymer-surfactant solutions [17–32]. Many studies revealed hydrophobically modified HEC exhibited no significant cytotoxic effect and represent a promising delivery vehicle for poorly water-soluble pharmaceutical active ingredients [32–36]. However, despite the growing body of literature concerning hydrophobically water-soluble cellulose derivatives, relatively little is known about morphology of polymeric micelles for amphiphilic cellulose derivatives.

It is well recognized that particle is crucial for the vivo fate of a drug delivery system. Understanding the relationship between the chemical structure of cellulose derivatives and the size of their possible polymeric micelles is very important to promote their potential utilization as carriers or microencapsulation agents for pharmaceuticals. In other words, the chemical structure of cellulose derivatives will
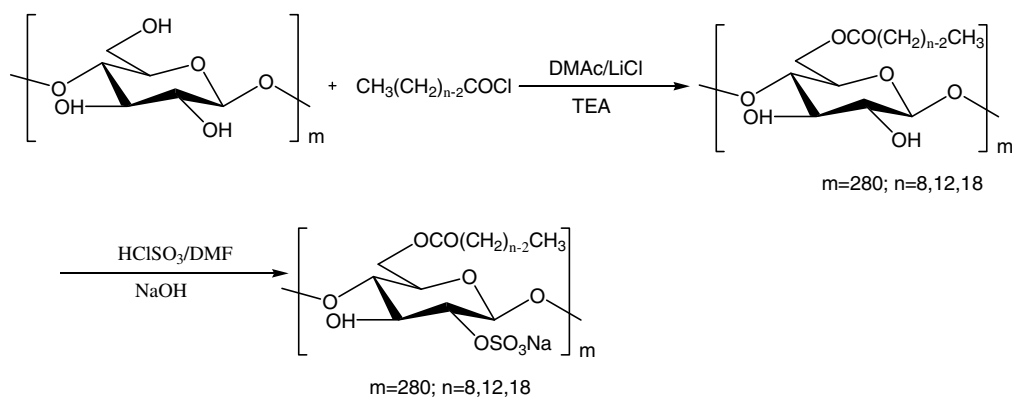
Scheme 1. Synthetic route of cellulose derivatives.

undoubtedly affect the surface activities of final amphiphilic cellulose derivatives. In this paper, three amphiphilic cellulose derivatives with different hydrophobic chains were synthesized. The synthetic pathway was depicted in Scheme 1[12]. The basic physico-chemical properties such as surface tension and cac were determined by the conventional Wilhelmy plate method. Effects of hydrophobic chains on the surface activity for their potential industry applications were also investigated, while their aqueous self-assembly behavior was studied using transmission electron microscopy (TEM) and dynamic laser scattering (DLS). In addition, rheological properties of obtained polymers were also discussed. These results will promote to exploit cellulose as more value-added products to improve the efficacy and safety of drug deliver system.

2. Experimental

2.1. Materials and measurements

Avicell PH-101 (Microcrystalline cellulose, degree of polymerization = 280) was purchased from Changshu Medial Supplements Co., Ltd. Jiangsu Province, P.R. China. Dimethyl acetoamide (DMAc), lithium chloride (LiCl), dimethyl formamide (DMF), triethylamine (TEA), pyridine were dried and purified before use. Octanoyl chloride, Lauroyl chloride, stearoyl chloride, methanol and chlorsulfanic acid were reagent grade and used without further purification.

2.2. Preparation of cellulose solution [37]

Stock solutions of LiCl in DMAc (9% w/w) were prepared by dissolving 4.2 g of reagent grade lithium chloride in 50 ml of *N,N*-dimethylacetamide at 80 °C. Solvent mixtures for each experiment were prepared immediately prior to use to minimize moisture uptake. Solvent-exchanged cellulose was added to the heated solvent. The mixture was allowed to stir with nitrogen sparging while cooling to room temperature.

2.3. Synthesis of cellulose-based amphiphilic polymer

The synthetic pathway of cellulose-based amphiphilic polymer was similar to our earlier literature [12]. Briefly, cellulose esters with different chain length (8, 12, 18) were synthesized in DMAc/LiCl.

Table 1
Synthesis conditions of cellulose derivatives

Samples	DS_{Alkyl}	$DS_{Sulfate}$
COS	0.74	0.34
CLS	0.57	0.25
CSS	0.78	0.15

Then these cellulose esters were suspended in DMF medium, and magnetically stirred overnight. Definite chlorsulfanic acid was added dropwise into with stirring at 0 °C under N_2 atmosphere. After completely dripped, the solution was kept in agitation for 1 h, and then the suspension of cellulose esters and DMF was added to the above solution. The mixture was stirred and heated to 50 °C for about 5 h under N_2 atmosphere, then the pH was adjusted to pH 7 by 20% NaOH in ice-water bath. Subsequently, the solution was dialyzed (MWCO 8000) against distilled water for 48 h and then lyophilized to give acylated cellulose sulfate as a white solid. The total synthesis pathway and DS were presented in Scheme 1 and Table 1, respectively. Conveniently, acylated cellulose sulfates with different hydrophobic chain length (8, 12, 18) were defined as follows: cellulose octanoate sulfate (COS), cellulose Laurorate sulfate (CLS) and cellulose stearoate sulfate (CSS).

2.4. Methods

2.4.1. Surface tension measurements

The surface tension at the air–water interface of aqueous solutions of cellulose derivatives was measured by the Wilhelmy plate method with Dynamic Contact Angle Analyzer (Germany) at 25 °C. The water used was ultrapure grade from Milli-Q plus system (Millipore, USA). All measurements were performed for at least 10^4 s in order to monitor the slow equilibration of the adsorption layers. The critical micelle concentration (cac) values were determined as the concentrations of samples corresponding to the inflection of the $\gamma(C)$ isotherms.

2.4.2. Dynamic light scattering (DLS)

The dynamic light scattering measurements were performed with an apparatus from brookhaven Instruments, Inc., model BI-9000AT, equipped with a laser (514.5 nm) and an autocorrelator at 25 °C. The sample solutions were filtered directly into cylindrical cells through membrane filtered (pore size 0.80 μm), the scattering angle was fixed at 90°.

2.4.3. Rheological measurements

The polymer solution viscosity was measured with a Bob/cup type rheometer Stress Tech-ETC2 (REOLOGICA Instruments Co., Ltd.) at 25 °C. The diameter of the cup was 25 mm and the gap between them was 1 mm. The rheometer was equipped with a reservoir to prevent sample drying during the measurements.

2.4.4. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was used to characterize morphology of polymeric micelles of cellulose derivatives in solution. Samples were immersed rapidly into the liquid ethane cooled by the liquid nitrogen. They were transferred into liquid nitrogen after about 5 s. The samples, after transferred into the chamber of the freeze-etching apparatus (BALZERS BAF-400D), were fractured at -120 °C, 3×10^{-7} mbar. After etched for 1 min, Pt-C was sprayed onto the fracture face at 45°, and then C was sprayed at 90°. The replicas when taken out of the chamber were achieved at milli-Q water. Then they were detected under the transmission electron microscope (PHILIPS-FEI TECNAI20).

3. Results and discussion

3.1. Synthesis of cellulose derivatives

A traditional method of introducing functional groups to cellulose backbone to prepare cellulose amphiphilic polymers was carried out by first hydrophilic modification of cellulose and then followed by the introduction of hydrophobic groups [8–11]. Because the hydrophobic modification of water-soluble was conducted in a heterogeneous system, the degree of substitution (DS) was very limited and difficult to controlled. According to our literature [12], a different approach to introduce functional groups was reported, in which hydrophobically cellulose derivatives with varying DS can be synthesized in homogenous solution using acyl chloride with varying chain length (8, 12, 18) as reported in previous reported literatures [37–39]. Because this reaction performed in DMAc/LiCl solution, DS was easily controlled. Cellulose long-chain fatty acid esters easily swell or dissolve in DMF, the sulfation can be conducted in nearly homogenous system. As can be seen from Table 1, the acylation (including Octanoylation, Lauroylation and stearoylation) could be well controlled by the mole ratio

of additional functional reagent such as Octanoyl chloride, Lauroyl chloride and stearoyl chloride to glucose unit. The pre-introduced hydrophobic groups would undoubtedly affect the substitution degree of next sulfation, the DSs of hydrophobically cellulose derivatives were designed as 0.7. Although the nearly DS of hydrophobically cellulose derivatives was used as precursor to be sulfated, the DS of sulfation could not achieved the same level due to steric effects of longer hydrophobic chains. These results indicated that our synthetic approach was a convenient method for preparing cellulose amphiphilic polymers.

3.2. Critical micelle concentration and surface tension

It is well known that amphiphilic polymers with a suitable hydrophilic/hydrophobic balance can form a micellar structure when exposed to a selective solvent. The amphiphilic nature of this cellulose derivative, consisting of hydrophilic and hydrophobic segments, provided an opportunity to form micelles in water. Critical micelle concentration is the minimum required concentration for a selected polymer to from micelles through self-assembling. Critical micelle concentration was determined by the conventional Wilhelmy plate method [12,40]. Fig. 1 showed the relationship between surface tension and concentration of cellulose amphiphilic polymers with three hydrophobic chain lengths (C_8, C_{12}, C_{18}). The critical micelle concentration (cmc) or critical aggregation concentration (cac) was obtained from the inflection point of the curve of surface tension versus concentration. Surface tension at cac (γ_{cac}) was also determined from the curve. Data were
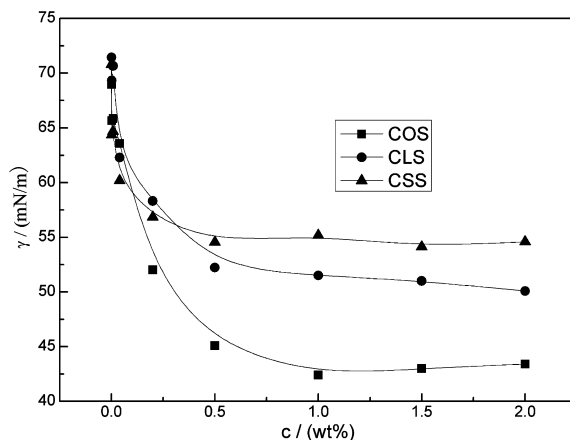

Fig. 1. Surface tension–concentration curve of cellulose derivatives.

summarized in Table 2. As shown in Fig. 1 and Table 2, cac values of polymeric micelles decreased from 0.28 to 0.08 wt%, corresponding surface tension increased from 44 to 55 mN/m when the hydro-

phobic chain length changed from 8 to 18. This indicated that the efficiency to reducing surface tension was significantly enhanced when the hydrophobic chain length increased, but corresponding surface tension increased also. These results suggested that these cellulose derivatives could be used as a potential, naturally polymeric surfactant.

Table 2
cac values and the corresponding surface tension of cellulose derivatives

Samples	cac (wt%)	γ_{cac} (mN/m)
COS	0.28	44
CLS	0.17	53
CSS	0.08	55

3.3. Particle size and morphology of the polymeric micelles

In order to investigate the effect of hydrophobic chain of cellulose derivatives on micelle-forming
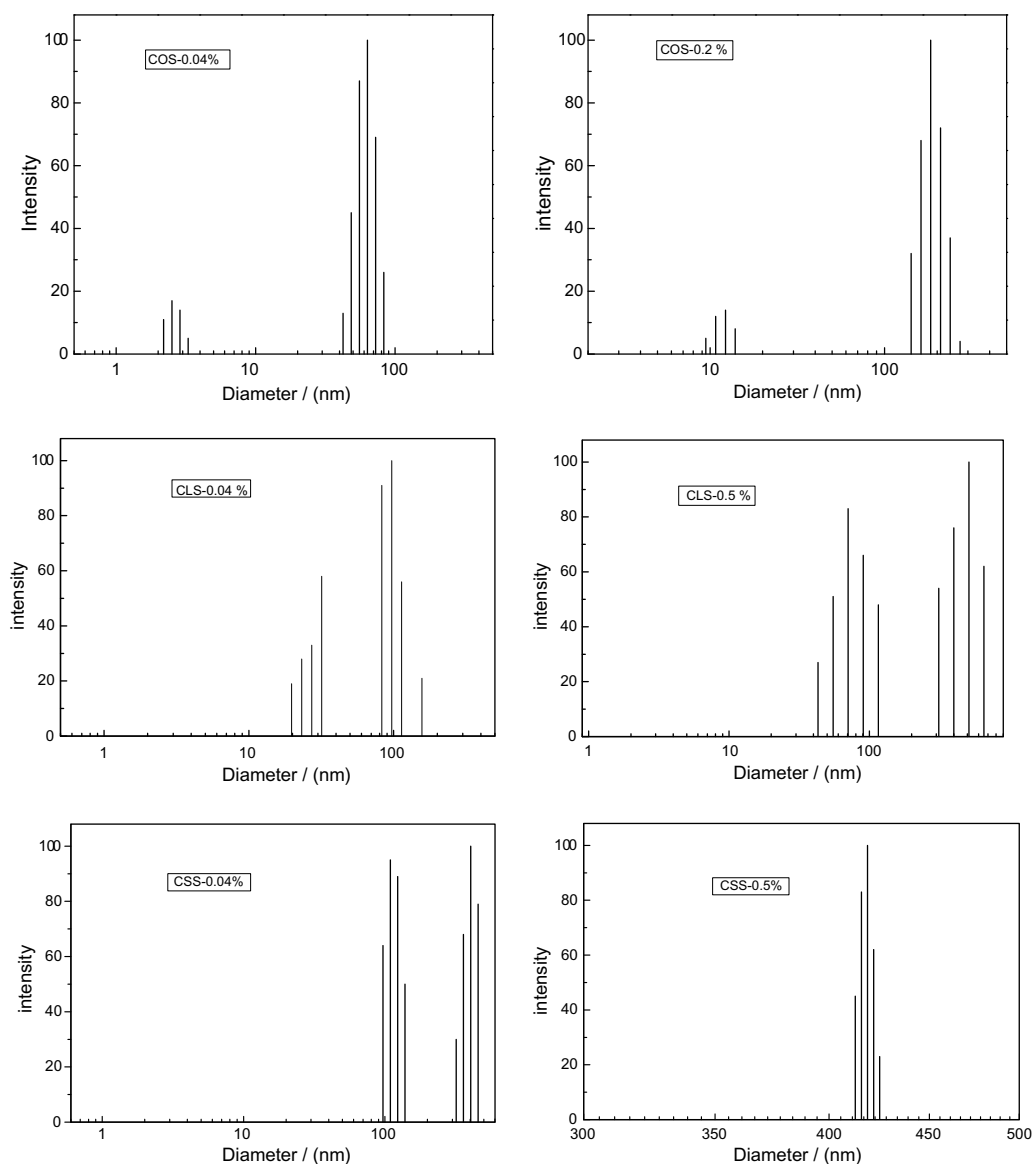

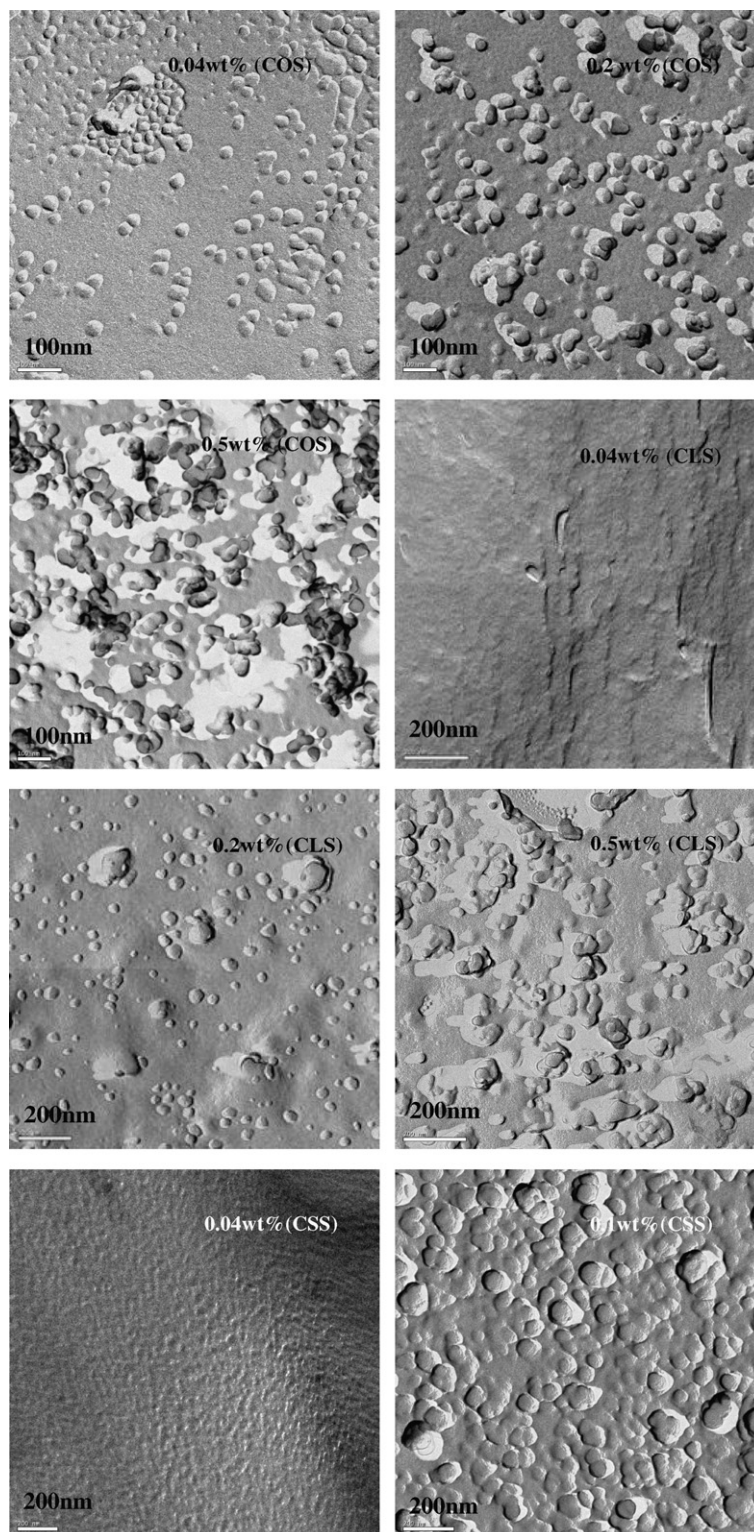Fig. 2. The hydrodynamic diameter distribution of three samples.

Fig. 3. TEM micrograph of micelles of three cellulose derivatives.

properties, three cellulose derivatives with the same hydrophilic head group and near same DS were tested. The aqueous self-assembly of amphiphilic polymers were monitored by TEM and DLS. Sizes of polymeric micelles were measured by DLS as function of concentration presented in Fig. 2 (see supporting information). As shown in Fig. 2, two peaks were detected for three tested polymers with a concentration of 0.04 wt% (low to cac), the first is related to polymeric micelles, and the second is related to larger aggregates. And with the increase of polymer concentration for three cellulose derivatives, average size of particle all increased in the experimental concentration ranges. The DLS data demonstrate that the micelle aggregates get larger as the hydrophobic chain increase, suggesting the elongation of hydrophobic side chain facilitates the growth of the hydrophobic core of polymeric micelles. The morphology of polymeric micelles was observed with freeze fracture TEM shown in Fig. 3 and data summarized in Table 3. As pre-

sented in Fig. 3, all three tested cellulose derivatives were able to self-aggregate and form polymeric micelles in pure water under the experimental conditions. And it could be confirmed that polymeric micelles were near spherical in shape. The diameter of the three polymeric micelles ranged from 20 to 67 nm. For COS, the diameter of polymeric micelles increased from 27.39 to 34.94 nm as the concentration increased from 0.04 to 0.2 wt%. For CLS, the diameter of polymeric micelles increased from 19.90 to 42.27 nm as the concentration increased from 0.04 to 0.2 wt%. While for CSS, the diameter of polymeric micelles increased from 23.52 to 65.95 nm as the concentration increased from 0.04 to 0.1 wt%. Interestingly, polymeric micelles of cellulose derivative with the hydrophobic chain lengths of C_{18} had larger particles size than the corresponding ones with the shorter hydrophobic chain lengths of C_8 and C_{12} as shown in Table 3, suggesting that the diameter of the nano-micelles was proportional to the length of hydrophobic chain under the experimental conditions. All pictures reveal that the micelles show spherical shape with a sharp boundary. The diameter of single particles is under 100 nm, which is much lower than that observed by light scattering. The possible reasons for this difference are as follows: first, larger aggregates in aqueous solution could be detected as polymeric micelles; second, only the core of the micelles can be observed by TEM as the chain density in the corona is probably not high enough to make visible contrast to the background [41]. Therefore, this

Table 3
Effects of hydrophobic chain length on size of cellulose derivative micelles[a]

Samples	Concentration (wt%)	Size of blank micelle (nm)
COS	0.2	34.94
CLS	0.2	42.27
CSS	0.1	65.95

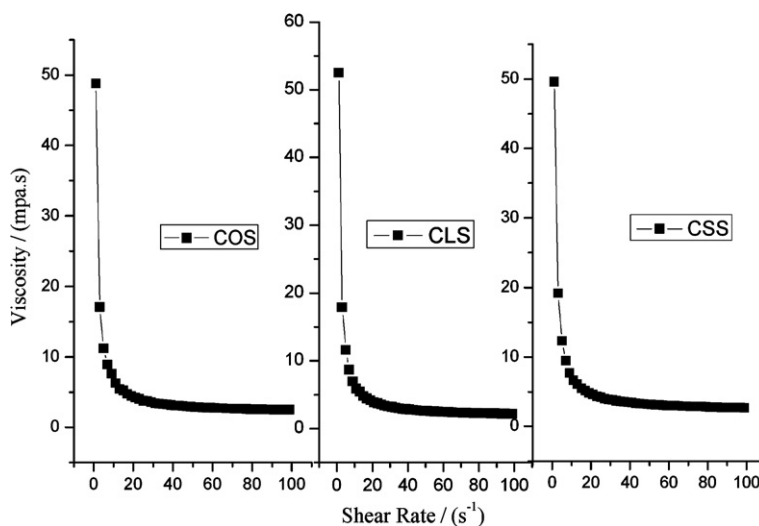[a] Micelle size is reported as an average diameter of micelles.

Fig. 4. Viscosity of cellulose derivative solutions as a function of shear rate.

observation failed to visualize the complex core–shell microstructure. Taken together, Figs. 2 and 3 indicate that cellulose derivatives can self-assemble into polymeric vesicle and changes in the chemical structures may alter their micelle-forming properties. Additional studies are necessary to further investigate this relationship between structure and functionality.

3.4. Effect of shear rates on apparent viscosity of cellulose derivatives

Cellulose derivatives exploited had been used in a wide variety of applications like food, pharma, cosmetic and other convenience products because of their specific solution properties. In this investigation, effects of shear rates on apparent viscosity of cellulose derivatives with different hydrophobic moieties were discussed. The microcrystalline structure of the cellulose is broken up by the substitution with sulfate and alkyl substituents and is converted into a soluble form, the hydrophobic character of the side chains leads to stronger intermolecular interactions in aqueous solution and to the formation of superstructures from association. The larger number of associations leads to three-dimensional physical cross-linking, which is primarily determining the flow behaviour at low shear rates. Fig. 4 plots the apparent viscosity of three cellulose derivatives solutions against shear rate at the concentration of 1.0 wt%. As shown in Fig. 4, with an increase in shear rate, cellulose derivatives first behaved like a pseudo-plastic property, and the apparent viscosity decreased sharply, indicating rapid damage to molecular networks built up by the relatively weak hydrophobic association. When the shear rate was higher than $40 \, s^{-1}$, apparent viscosity remained at about 5 mPa s and became independent on the shear rate. The superstructures caused by hydrophobic interactions are degraded by the increasing shear force input until the viscosity has attained the level of the zero-shear viscosity [42–44]. The length of hydrophobic tail attached to the polymer backbone had not any pronounced influence on rheological properties of cellulose derivatives under the experimental conditions as seen in Fig. 4. This was attributed to the fact that hydrophobic interactions among hydrophobic residues compete with repulsive electrostatic interactions among charged segments in aqueous solution of amphiphilic polyelectrolytes [45–53]. The concentration of three amphiphilic polymers was all at 1.0 wt% (far above

the cac), polymer chains may entangle and three-dimensional physical cross-links formed due to interchain hydrophobic associations as mentioned above. The strong interchain associations form large aggregates (a network structure of polymer chains) will contribute significantly to the thickening or the increase of viscosity. The association is more favorable for the amphiphilic polymers with shorter alkyl lengths. On the other hand, three polymers possessed different alkyl chain length and different charge densities (or $DS_{Sulfate}$) as shown in Table 1. The tendency of viscosity decrease induced by hydrophobic interactions polymers with alkyl chains compensated the increase of viscosity by repulsive electrostatic interactions among charged segments with sodium sulfate groups. But viscosity reflects only global changes in the polymer size. Thus, plots of viscosity versus the shear rate for three polymers with different alkyl chains gave almost same profile. The addition of low-molar-mass surfactants and salt can prevent the hydrophobic interactions that result in the formation of intermolecular superstructures. Further research about effects of surfactant and electrolytes added to the rheological behavior of cellulose derivatives was under way in our lab.

4. Conclusions

The above results indicated that cellulose after amphiphilic modifications had favorable properties such as surface activities and rheological properties. The *cac* decreased from 0.28 to 0.08 wt% and the corresponding surface tension increased 44 to 55 mN/m when the hydrophobic chain length changed from 8 to 18. The hydrophobic chain length of 12 was between C_8 and C_{18}. These cellulose derivatives were able to self-aggregate and form nanosized polymeric micelles of spherical shape in pure water under the experimental conditions. The diameter of the nano-micelles was proportional to the length of hydrophobic chain, but the length of hydrophobic tail had not any pronounced influence on rheological properties under the experimental conditions. These results suggested that this amphiphilic polymer might find use as surfactant and a potential drug carrier. Further research is required to investigate the possible application of these cellulose nano-materials in controlled release and surfactant for improving the stability, safety and consumer acceptability, thus benefiting human health.

Acknowledgment

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.reactfunctpolym.2008.02.004.

References

[1] L.M. Landoll, J. Polym. Sci. Polym. Chem. Ed. 20 (1982) 443.

[2] A.C. Sau, L.M. Landoll, Polymers in aqueous media: performance through association, in: J.E. Glass (Ed.), Advances in Chemistry Series 223, American Chemical Society, Washington, DC, 1989.

[3] R.A. Gelman, H.G. Barth, Water soluble polymers: Beauty with performance, in: J.E. Glass (Ed.), Advances in Chemistry Series 213, American Chemical Society, Washington, DC, 1986.

[4] R. Tanaka, J. Meadows, G.O. Phillips, Carbohydr. Polym. 12 (1990) 443.

[5] I. Srokova, P. Talaba, P. Hodul, A. Balazova, Tenside Surf. Det. 35 (1998) 342.

[6] P. Talaba, I. Srokova, A. Ebringerova, P. Hodul, A. Marcincin, J. Carbohydr. Chem. 16 (1997) 573.

[7] I. Srokova, V. Tomanova, A. Ebringerova, A. Malovikova, T. Heinze, Macromol. Mater. Eng. 289 (2004) 63.

[8] V. Rosilio, G. Albrecht, A. Baszkin, L. Merle, Colloid. Surf. B: Biointerf. 19 (2000) 163.

[9] T. Aubry, M. Moan, J. Rheol. 38 (1994) 1681.

[10] T. Aubry, M. Moan, J. Rheol. 40 (1996) 441.

[11] L. Merle, D. Carpentier, G. Mocanu, S. Chapelle, Eur. Polym. J. 35 (1999) 1.

[12] Y.P. Wei, Fa Cheng, Carbohydr. Polym. 68 (2007) 734.

[13] I.F. Uchegbu, A.G. Schatzlein, L. Tetley, A.I. Gray, J. Sludden, S. Siddique, E. Mosha, J. Pharm. Pharmacol. 50 (1998) 453.

[14] W. Wang, A.M. McConaghy, L. Tetley, I.F. Uchegbu, Langmuir 17 (2001) 631.

[15] D.E. Discher, A. Eisenberg, Science 297 (2002) 967.

[16] M. Antonietti, S. Forster, Adv. Mater. 15 (2003) 1323.

[17] R. Tanaka, J. Meadows, P.A. Willians, G.O. Phillips, Macromolecules 25 (1992) 1304.

[18] U. Kastner, H. Hoffmann, R. Donges, R. Ehrler, Colloid. Surf. A 82 (1994) 279.

[19] U. Kastner, H. Hoffmann, R. Donges, R. Ehrler, Colloid. Surf. A 112 (1996) 209.

[20] A. Goldszal, S. Costeux, M. Djabourov, Colloid. Surf. 112 (1996) 141.

[21] A.J. Dualeh, C.A. Steiner, Macromolecules 23 (1990) 251.

[22] A.J. Dualeh, C.A. Steiner, Macromolecules 24 (1991) 112.

[23] C.A. Steiner, J. Appl. Polym. Sci. 42 (1991) 1493.

[24] C.G. Varelas, C.A. Steiner, J. Polym. Sci. Part B: Polym. Phys. 30 (1992) 1233.

[25] C.G. Varelas, A.J. Dualeh, C.A. Steiner, in: P. Dubin, J. Bock, R. Davis, D.N. Schulz, C. Thies (Eds.), Macromolecular Complexes in Chemistry and Biology, Springer-Verlag, Berlin, 1994, p. 63.

[26] K. Thuresson, S. Nilsson, B. Lindman, Langmuir 12 (1996) 530.

[27] K. Thuresson, B. Nystrom, G. Wang, B. Lindman, Langmuir 11 (1995) 3730.

[28] K. Thuresson, O. Soderman, P. Hansson, G. Wang, J. Phys. Chem. 100 (1996) 4909.

[29] G.Q. Zhao, C.C. Khin, S.B. Chen, B.H. Chen, J. Phys. Chem. B 109 (2005) 14198.

[30] I. Lliopoulos, U.J. Olsson, J. Phys. Chem. 98 (1994) 1500.

[31] K. Loyen, R. Lliopoulos, R. Audebert, U. Olsson, Langmuir 11 (1995) 1053.

[32] K. Loyen, R. Lliopoulos, U. Olsson, R. Audebert, Prog. Colloid. Polym. Sci. 98 (1995) 47.

[33] Q.R. Cao, Y.W. Choi, J.H. Cui, B.J. Lee, J. Control. Release 108 (2005) 351.

[34] O. Chambin, D. Champion, C. Debray, M.H. Rochat-Gonthier, M. Le Meste, Y. Pourcelot, J. Control. Release 95 (2004) 101.

[35] Y. Suzuki, Y. Makino, J. Control. Release 62 (1999) 101.

[36] M.F. Francis, M. Piredda, F.M. Winik, J. Control. Release 93 (2003) 59.

[37] C.L. McCormick, D.K. Lithatowich, J. Polym. Sci. Polym. Lett. Ed. 17 (1979) 479.

[38] G. Samaranayake, W.G. Glasser, Carbohydr. Polym. 22 (1993) 1.

[39] J.E. Sealey, G. Samaranayake, J.G. Todd, J. Polym. Sci. Part B: Polym. Phys. 34 (1996) 1613.

[40] T. Ihara, T. Nishioka, H. Kamitani, T. Kitsuki, Chem. Lett. 33 (2004) 1094.

[41] X.F. Yuan, M. Jiang, H.Y. Zhao, M. Wang, Y. Zhao, C. Wu, Langmuir 17 (2001) 6122.

[42] A. Maestro, C. Gonzalez, J.M. Gutierrez, J. Rheol. 46 (2002) 1445.

[43] L. Qin, Y. Ye, R.H. Huang, J. Appl. Polym. Sci. 100 (2006) 3346.

[44] C. Clasen, W.M. Kulicke, Prog. Polym. Sci. 26 (2001) 1839.

[45] H. Yamamoto, I. Tomatsu, A. Hashidzume, Y. Morishima, Macromolecules 33 (2000) 7852.

[46] T. Noda, Y. Morishima, Macromolecules 32 (1999) 4631.

[47] Y. Morishima, S. Nomura, T. Ikeda, M. Kamachi, Macromolecules 28 (1995) 2874.

[48] M. Seki, Y. Morishima, Macromolecules 25 (1992) 6540.

[49] Y. Morishima, M. Tsuji, M. Seki, M. Kamachi, Macromolecules 26 (1993) 3299.

[50] H. Yamamoto, M. Mizusaki, K. Yoda, H. Yamamoto, Macromolecules 31 (1998) 3588.

[51] H. Yamamoto, Y. Morishima, Macromolecules 32 (1999) 7469.

[52] Y. Umar, B.F. Abu-Sharkh, S. Asrof Ali, Polymer 46 (2005) 10709.

[53] H. Widad, D. Michel, S. Michel, L. Didier, L. Picton, V. Rosilio, J. Colloid. Interf. Sci. 281 (2005) 316.