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Host–guest chemistry of cyclodextrin carbamates and cellulose derivatives in aqueous solution

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ABSTRACT

Supramolecular polymer micelles were prepared on basis of the inclusion complexation between cyclodextrin carbamates and cellulose derivatives in aqueous media. Cyclodextrin carbamates were synthesized by microwave-assisted method from cyclodextrin and urea. The urea modified cyclodextrin shows the higher yield than the physical mixture of urea/cyclodextrin in the micellization with cellulose derivatives. The supramolecular structure of the core–shell micelles was demonstrated by ^{1}H NMR spectra, TEM images, and fluorescence spectra. The drug release behavior of the supramolecular polymer micelles was evaluated using prednisone acetate as a model drug. The drug loaded micelles showed steady and long time drug release behavior. With these properties, the supramolecular polymer micelles are attractive as drug carriers for pharmaceutical applications.

1. Introduction

Supramolecular self-assembly has been used to construct various supramolecular architectures, such as micelles, vesicles, hydrogels, nanofibers, and nanotubes through non-covalent interactions (Anraku, Kishimura, Yamasaki, & Kataoka, 2013; Chen et al., 2011; Chen, 2012; Okumura & Ito, 2001; Yan, Xin, Zhou, Yin, & Yuan, 2011; Zhu, Liu, & Du, 2013). Many kinds of non-covalent interactions, such as hydrogen bonding, ionic interactions, Van der Waals interactions, and hydrophobic interactions can be used for the design and construction of supramolecular architectures. The host-guest interaction, the most important interaction in biological systems, has been widely studied since the rising of the concept of supramolecular chemistry (Liao et al., 2010; Nepogodiev & Stoddart, 1998; Tao et al., 2012; Yan et al., 2013).

Cyclodextrins (CDs) are cyclic compounds consisting of six, seven, and eight α-1,4-coupled D-glucose units (Chen, Zhang, & Liu, 2010; Wenz, Han, & Muller, 2006), which are named α-cyclodextrin, β-cyclodextrin, and γ-cyclodextrin, respectively. Due to the rigid, well-defined ring structure and the ability to bind various compounds, natural CDs and their derivatives were chosen as host for the construction of various supramolecular architectures (Kulkarni, DeFrees, Hyun, & Thompson, 2012; Wang et al., 2012). Recently, CD-based supramolecular polymer inclusion complexes composed of multiple CD rings threaded on a polymer chain with or without bulky end-caps, have attracted great attention for the development of supramolecular materials (Huang & Gibson, 2005; Tamesue, Takashima, Yamaguchi, Shinkai, & Harada, 2010; Zhao, Zhang, & Ma, 2006). Various polymers have been reported to form inclusion complexes with CD, including polyethers, polyanilines, polyesters, polyolefins, and so on (Dong, Kai, Pan, Cao, & Inoue, 2007; Harada & Kamachi, 1990; Kawaguchi, Nishiyama, Okada, Kamachi, & Harada, 2000; Yang, Ni, & Li, 2009; Yoshida, Shimomura, Ito, & Hayakawa, 1999). The insolubility of the inclusion complexes in most solvents, especially water, restricts the potential applications. Dong reported a one-pot method to construct α-CD/poly(ε-caprolactone) (PCL) supramolecular polymer micelles, by using urea or α-CD derivatives to eliminate the hydrogen bonds between the α-CDs, resulting the water-soluble inclusion complexes (Dong et al., 2008).

Due to the biodegradability, biocompatibility, and widely chemical modifying capacity, cellulose has been used in pharmaceutical applications, agricultural applications, cosmetics, and coating since cellulose was first reported by French chemist Anselme Payen in 1839 (Chang & Zhang, 2011; Edgar et al., 2001; Kang, Liu, & Huang, 2013; Wang et al., 2011). For instance, the L-phenylalanine triggering supramolecular polymer micelles were constructed from ethylcellulose-graft-poly(ε-caprolactone) and α-CD derivatives via host-guest and hydrophobic interactions (Dong et al., 2011). Cellulose and cellulose derivatives have also considered as guest polymer for the design of novel inclusion complexes with CDs. More recently, we found that methylcellulose

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(MC) was hydrophobic compared with cyclodextrin and was able to penetrate the hydrophobic cavity of host β-cyclodextrin to form amphiphilic supramolecular polymers β-CD/MC (Du et al., 2012).

In this paper, we describe a facile and environmentally friendly method for the synthesis of cyclodextrin carbamates and the preparation of supramolecular polymer micelles based on cyclodextrin carbamates/cellulose derivatives. Cyclodextrin carbamates were synthesized by microwave-assisted method from cyclodextrin and urea under solvent-free and catalyst-free conditions. The micellization of the inclusion complexation between cyclodextrin carbamates and cellulose derivatives was characterized by ^{1}H NMR spectra, FT-IR spectra, TEM images, and fluorescence spectra. The drug release behavior of the supramolecular polymer micelles was evaluated using prednisone acetate as a model drug.

2. Experimental

2.1. Materials

α-cyclodextrin (α-CD) was purchased from Acros. β-cyclodextrin (β-CD), methyl cellulose M450 (MC), ethyl cellulose M70 (EC), cellulose acetate (CA), and urea was purchased from Shanghai Chemical Reagent Co. Ltd. γ-cyclodextrin (γ-CD) and cellulose acetate butyrate (CAB) was supplied by Aladdin Chemistry Co. Ltd. All the other reagents and solvents were commercially available and used without further purification.

2.2. Preparation of cyclodextrin carbamates (U-CD)

Cyclodextrin carbamates were synthesized as follows: the mixtures of cyclodextrin with certain amount of urea were put into mortar and ground. Then the mixture was irradiated at predetermined microwave power for 2–10 min. The crude product was dissolved in water and precipitated in excess ethanol. After that, it was filtrated and the obtained powder was dried in vacuum.

2.3. Formation of supramolecular micelles

The solution of CD/urea (or U-CD) in 10 mL water was added dropwise to a stirred solution of MC (or EC, CA, CAB) in 15 mL DMSO at 60 °C, and the resulting mixture was stirred at 60 °C for 24 h, small amounts of precipitates were removed by centrifugation after cooling the mixture to room temperature. The solvent and excess small molecules in the mixture were removed by dialysis against distilled water. The solution was freeze-dried before characterization. For prednisone acetate loaded supramolecular polymer micelles, the procedure is the same as the above, using a solution of cellulose derivative and prednisone acetate in DMSO. The yield of the supramolecular micelles was calculated based on the following equation:

$$\text{Yields}\ \ (\%) = \frac{W_t}{W_o} \times 100\%$$

where W_t represents the weight of obtained micelles, and W_o is the weight of fed cellulose derivative.

2.4. Fluorescence measurements

The fluorescence experiment using pyrene as a hydrophobic fluorescent probe, was recorded on a RF-5301PC (Shimadzu) spectrofluorophotometer. Aliquots of pyrene solutions (6×10^{-6} M in acetone, 500 μL) were added into a series of volumetric flask. The acetone was allowed to evaporate. The solution of redissolved lyophilized micelles were added into the flasks and diluted till the calibration mark using distilled water to achieve the desired concentrations rang from 1 mg/L to 1000 mg/L. Then ultrasonic dispersion for 10 min, the samples were stored at room temperature for 24 h to reach the equilibrated solubilization of pyrene in the aqueous phase. Steady-state fluorescence emission spectra were recorded at 310 nm excitation wavelength with a bandwidth (ex) of 3 nm. For excitation spectra, the emission wavelength was 390 nm and bandwidth (em) was 3 nm, unless otherwise stated.

2.5. In vitro drug release

4 mg of lyophilized sample of drug loading micelle was dissolved into 2 mL distilled water and placed into dialysis bag (dialysis membrane, MWCO 3500), which was immerged into 50 mL distilled water at 37 °C. 2 mL of release medium were removed periodically from the solution as well as the volume of solution was preserved constantly by adding 2 mL distilled water. The drug loading content (DLC) was measured by UV absorbance method. The quantity of drug released from the micelle was calculated from the UV absorbance of the solution at 242 nm. The cumulative drug release was calculated from the following equation:

$$\text{Cumulative drug release}\ \ (\%) = \frac{M_t}{M_0} \times 100\%$$

where M_t represents the amount of drug released from micelles at time t, and M_0 estimates by drug loading content.

2.6. Measurements

NMR spectra were recorded on a Mercury VX-300 spectrometer using DMSO-d6 (TMS as the internal standard) and D_2O as solvents. FT-IR spectra were recorded on a Thermo IS10 spectrometer. Fluorescence spectra were measured on a RF-5301PC (Shimadzu) spectrofluorophotometer using pyrene as a fluorophore. TEM images were recorded on a JEM-2100 (HR) transmission electron microscope at an acceleration voltage of 200 kV, using 0.1% (w/v) phosphotungstic acid as negative staining reagent. Dynamic light scattering (DLS) measurements were conducted on a light scattering spectrometer (ALV/SP-125, ALV, Germany) equipped with an ALV-5000/E correlator and a He–Ne laser (at $\lambda = 632.8$ nm) at scattering angles $\theta = 90°$. All of the test solutions made optically clean by filtration through 0.45 μm millipore filters. The MALDI-TOF-MS spectra were recorded with an Axima TOF2 mass spectrometry (Shimadzu, Kyoto, Japan). The instrument was equipped with a 337 nm nitrogen laser with a 3 ns pulse width. The detection was performed in positive ion reflector mode with an accelerating voltage of 20 kV. Typically, 500 laser shots were averaged to generate each spectrum. The UV absorbance was recorded on SP-752 UV spectrophotometer (Shanghai spectrum Corp.). X-Ray diffraction (XRD) was recorded on a Bruker D8-advance with the scan speed of 4° min^{-1}. Elemental analysis (EA) of C, H and N was carried out with Elementar Analysensysteme GmbH VarioEL III (German). A 2.45 GHz multimode microwave oven (WBFY-201) with a maximum output power of 800 W was applied in this study.

3. Results and discussion

3.1. Synthesis and characterization of cyclodextrin carbamates (U-CD)

Cyclodextrin carbamates were synthesized from cyclodextrins and urea under microwave irradiation. The mixture of cyclodextrin/urea was ground for 10 min, and then heated in a microwave oven at 240 W for several minutes. Fig. 1 shows ^{13}C NMR spectra of the cyclodextrin carbamates and urea. Besides the chemical shifts of the cyclodextrin, all of the cyclodextrin carbamates samples display a remarkable signal at 159.0 ppm typically for the carbonyl

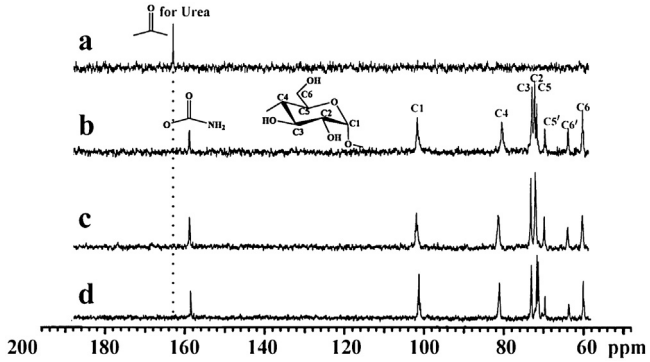

Fig. 1. ^{13}C NMR spectra of the cyclodextrin carbamates and urea. (a) urea, (b), U-γ-CD, (c) U-β-CD, and (d) U-α-CD.

carbon (Guo, Zhou, Wang, Zhang, & Lin, 2010). The carbon chemical shift of C=O for urea was at 162.9 ppm. Fig. S1 shows the FT-IR spectra of U-α-CD, U-β-CD, U-γ-CD, and their native CD. In comparison with native CD, cyclodextrin carbamates have an obvious new absorption band at 1713 cm^{-1}, which is assigned to the stretching vibration of the carbonyl (C=O) in the base of urethane (Nada, Kamel, & El-Sakhawy, 2000). The absorption near 1617 cm^{-1} is the characteristic band for —CO—NH— group. These results indicate that urea has reacted with the CD to form cyclodextrin carbamate. Furthermore, as shown in the Fig. S2, the absorption band at 1713 cm^{-1} gradually increases with the nitrogen content of the cyclodextrin carbamate. And the structure of cyclodextrin carbamate was further confirmed by MALDI-TOF MS (Fig. S3). The results mentioned above verify the successful introduction of carbamate groups to the cyclodextrin.

The influence of microwave power and reaction time were also investigated (Table 1). The reaction took long time at 80 W, and was accompanied with carbonization and cross-linking at a relatively high power level (>400 W). The influence of irradiation time was investigated with the microwave power of 240 W for four reaction times (2, 5, 8, and 10 min). The nitrogen content of the cyclodextrin carbamates increased from 0.375% to 3.039% with the reaction time from 2 to 10 min. Fig. S4 shows the ^{13}C NMR spectra of U-β-CD with different irradiation time. Signal at 159.0 ppm typically for the carbonyl carbon gradually increases with the reaction time. The influence of microwave power on the reaction was investigated with an irradiation time of 5 min. The data summarized in Table 1 show that the nitrogen content of the cyclodextrin carbamates increased from 0.346% to 3.324% with microwave power from 80 to 400 W. The ^{13}C NMR spectra of U-β-CD (Fig. S5) also give evidence of increase of nitrogen content of the cyclodextrin carbamates with microwave power. All the evidences show that cyclodextrin carbamates with different degree of substitution can be prepared by controlling microwave power or reaction time.

Table 1
Reaction conditions and nitrogen content (%) of cyclodextrin carbamates.

No.	Power (W)	*t* (min)	Yield (%)	*N* (%)
1	240	2	68.3	0.375
2	240	5	76.2	2.149
3	240	8	94.5	2.633
4	240	10	94.9	3.039
5	80	5	67.5	0.346
6	400	5	98.7	3.324
7	400	2	68.4	1.063

Yields (%) = $W_t/W_o \times 100\%$, where W_t represents the weight of cyclodextrin carbamates, and W_o is the weight of fed cyclodextrin.

Table 2
Yields of supramolecular polymer micelles with different materials.

	α-CD/Urea	U-α-CD	β-CD/Urea	U-β-CD	γ-CD/Urea	U-γ-CD
MC	34	63.2	88	121	70	93.8
EC	20.5	44.6	30	40.6	47.5	55.5
CA	10	24.1	22.5	29	26	61.5
CAB	63.5	18.7	46	44.5	46	70.1

The yield was calculated based on the equation: yield (%) = weight of obtained micelle/weight of added cellulose derivative × 100%.

3.2. Preparation and characterization of supramolecular polymer micelles

Supramolecular polymer micelles were prepared by dialysis method. As listed in Table 2, the yield of U-CD micelles was higher than that of CD/urea micelles. With the introduction of carbamate groups, the more hydrogen bonds and crystalline structures of the native cyclodextrin are destroyed than with free urea (Fig. S6), which suppresses the formation of crystallized pseudo-polyrotaxanes. Furthermore, for MC micelles, U-β-CD shows the highest yield; while for EC, CA, CAB micelles, U-γ-CD has highest yield. That is a good correlation between the sizes of the CD cavities and the cross-sectional areas of the polymers (Harada, Hashidzume, Yamaguchi, & Takashima, 2009).

The representative FT-IR spectra of U-γ-CD/EC micelle, the components, and the physical mixture are shown in Fig. S7. The vibration absorption bands for the C—H of EC appear at 2975 and 2787 cm^{-1}. The characteristic bands of U-γ-CD around 1713 and 1617 cm^{-1} were also found in the spectrum. These results provide direct evidence of the presence of both EC and U-γ-CD components in the micelle. The C=O band of U-γ-CD at 1713 cm^{-1} shifted to 1716 cm^{-1} after the micellization. A new band appeared at 1611 cm^{-1}, while the changes in the relative intensity of multiple peaks in 1375 and 800–1100 cm^{-1} can be observed in the micelle compared with other components. All these results indicate the micelles were prepared by self assemblies of U-γ-CD and EC through host-guest interactions (Lu, Shin, Nojima, & Tonelli, 2000).

The core–shell structure of the micelles is established based on evidence from ^1H NMR study and the fluorescence spectra of pyrene. Fig. 2 shows the ^1H NMR spectra of the U-γ-CD/EC micelle in DMSO-d6 and D_2O. Resonances associated with both the hydrophobic EC block and the hydrophilic inclusion complex block were clearly detected in DMSO-d6, a good solvent for both the U-γ-CD and EC parts. Whereas micelles in deuterated water displayed clear signals for the U-γ-CD and much diminished signals for the EC part. This result indicates that the cores of the assemblies are mainly composed of EC chains with limited mobility, and the hydrophilic inclusion complex block is the fully hydrated corona. This result provide direct spectroscopic evidence

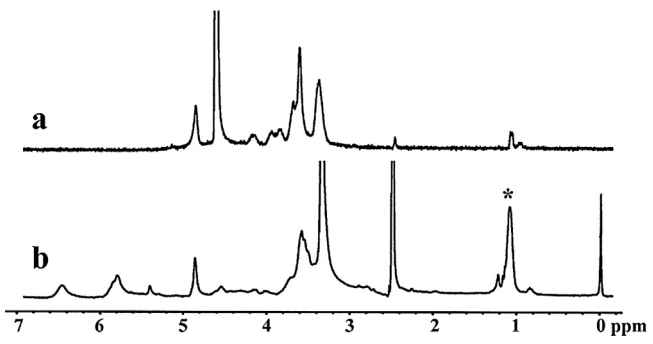

Fig. 2. ^1H NMR spectra of the U-γ-CD/EC micelle in D_2O (a), and DMSO-d6 (b) (*represent the signals assigned to EC).

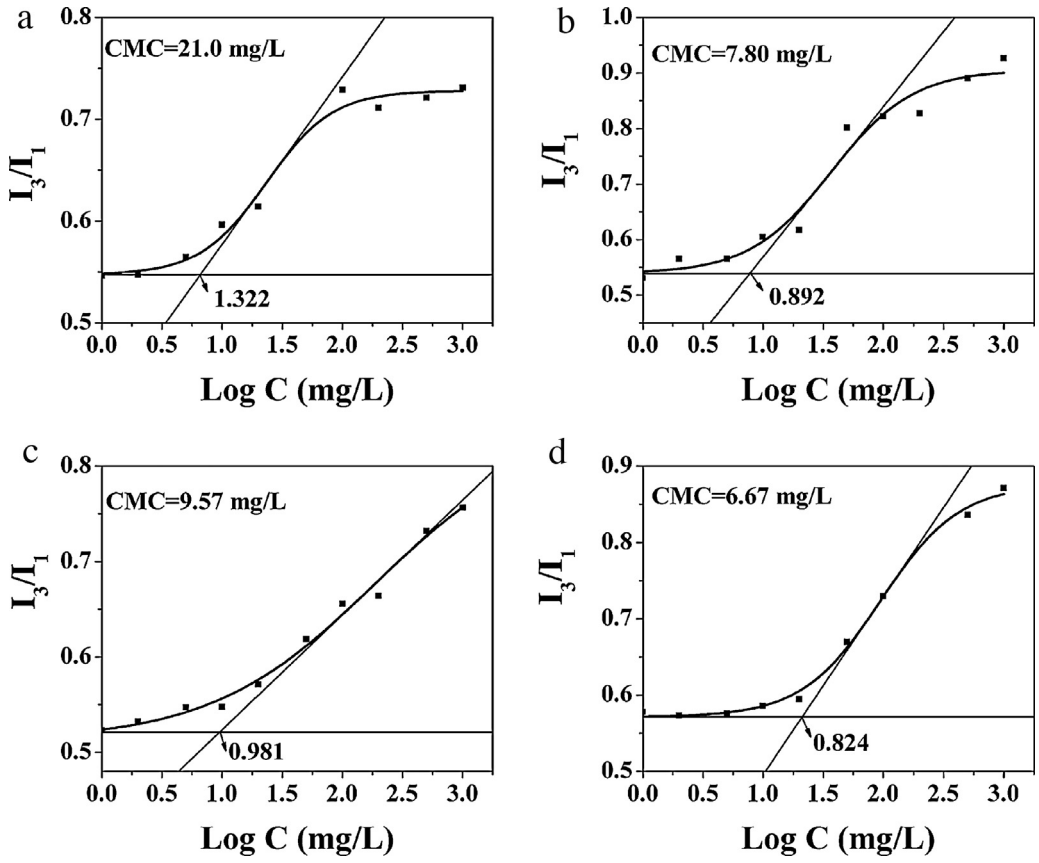

Fig. 3. Plots of fluorescence intensity ratio I_3/I_1 from pyrene emission spectra vs. log C for (a) U-β-CD/MC micelle, (b) U-γ-CD/EC micelle, (c) U-γ-CD/CA micelle, and (d) U-γ-CD/CAB micelle.

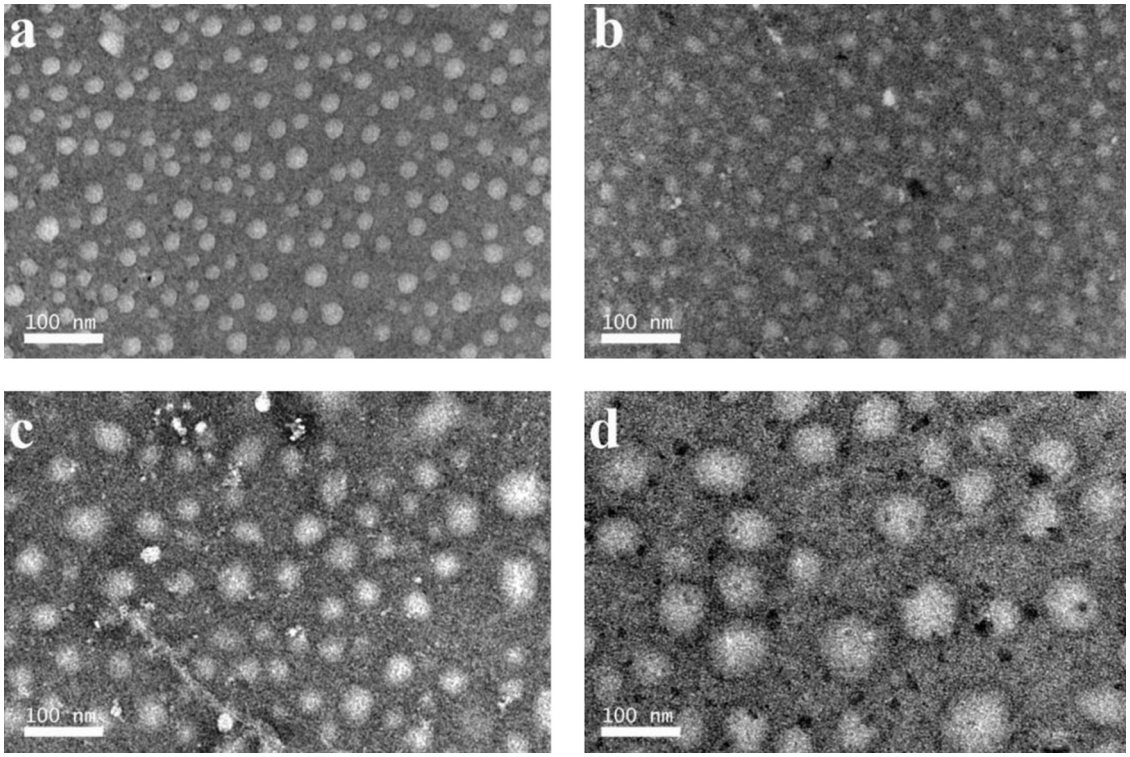

Fig. 4. TEM images of micelles stained by 0.1% phosphotungstic acid, (a) U-β-CD/MC micelle, (b) U-γ-CD/EC micelle, (c) U-γ-CD/CA micelle, and (d) U-γ-CD/CAB micelle.

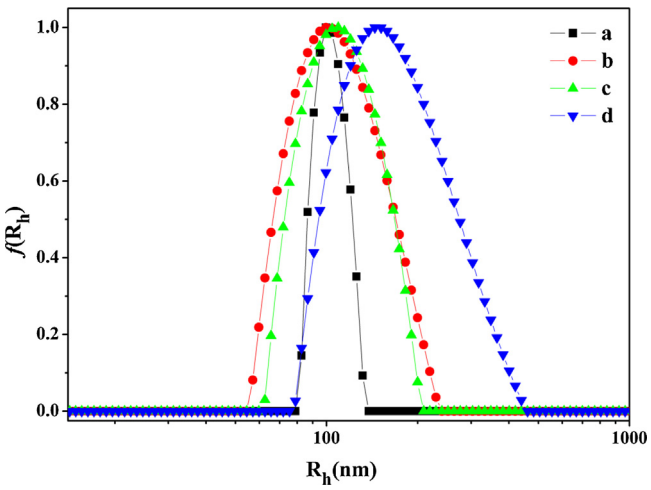

Fig. 5. R_h of the self-assembled micelles, (a) U-β-CD/MC micelle, (b) U-γ-CD/EC micelle, (c) U–CD/CA γ micelle, and (d) U-γ-CD/CAB micelle.

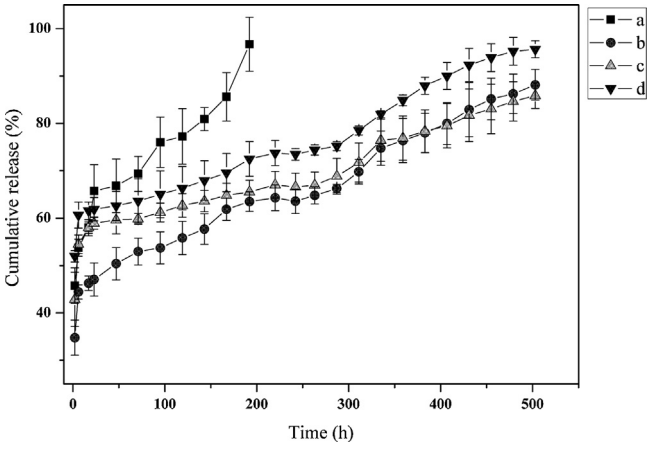

Fig. 6. Drug release behavior of drug-loading micelles (a) U-γ-CD/MC micelle, (b) U-γ-CD/EC micelle, (c) U-γ-CD/CA micelle, and (d) U-γ-CD/CAB micelle.

for the formation of a core–shell structure under aqueous medium (Danquah, Fujiwara, & Mahato, 2010; Yuen & Tam, 2013).

The self-assembly behavior of the cyclodextrin carbamate/cellulose derivative micelles were also investigated by fluorescence excitation spectra and emission spectra using pyrene as a fluorescence probe. Fig. S8a shows the fluorescence-excitation spectra of pyrene probe in U-γ-CD/EC micelles at different concentrations in water. The fluorescence intensity increased with the concentration of micelle solution, and the (0,0) absorption band of pyrene shifted from 334 nm to 337 nm was observed. The red shift is induced by the transfer of pyrene molecules from water to the hydrophobic region, suggesting the micellization of U-γ-CD/EC (Cho & Allcock, 2009).

The fluorescence spectrum of pyrene has five characteristic peaks, and the variation in the intensity ratio of the third I_3 (383 nm) to the first vibrational peak I_1 (373 nm) can be used as a sensitive factor to represent the local polarity of the microenvironment (Kalyanasundaram & Thomas, 1977). The value of I_3/I_1 is close to the value of pyrene in water (0.63) at low concentrations (Fig. 3), and then increases with the concentration of micelles. This result indicates that the cellulose derivative complex with cyclodextrin carbamate spontaneously formed micelles in aqueous solutions and this enabled the pyrene to locate in the hydrophobic core of the micelles.

We further confirmed the micellization by examining their critical micelle concentrations (CMCs) using fluorescence spectroscopy (Fig. 3). The CMCs can be calculated from the change of the intensity ratio (I_3/I_1) of pyrene fluorescence emission spectra in the presence of micelle by means of the intercept of two straight lines (Aguiar, Carpena, Molina-Bolívar, & Carnero Ruiz, 2003). It can be obviously observed that the CMC values of these micelles were relatively low (ranging from 6.7 mg/L to 21 mg/L).

The morphologies of the self-assembled micelles were investigated by TEM. The TEM images (Fig. 4) show that the morphologies of these micelles, regardless of the different content in the assemblies, were observed to be nearly spherical. The average particle size of the micelle diameters ranged from 20 to 60 nm, increased with the cross-sectional areas of the polymers. The size of these micelles in aqueous solution was analyzed by DLS. As shown in Fig. 5, the mean size is 102.9 nm, 107.9 nm, 110.8 nm and 166.3 nm for micelles of U-β-CD/MC, U-γ-CD/EC, U-γ-CD/CA, and U-γ-CD/CAB, respectively. The difference between the two measurements was ascribed to the fact that the former was the size in dry state, whereas the latter was the size in aqueous solution. Similar results were already reported in literature (Xue et al., 2009).

3.3. *In vitro drug release*

The drug release of micelles was carried out at 37 °C and monitored using a UV spectrophotometer at 242 nm. Prednisone acetate, an anti-inflammatory drug, was selected as a model drug. We chose four kinds of micelles for the drug release investigation. The drug loading content is 2.2%, 5.9%, 7.9%, and 6.8% for U-β-CD/MC micelle, U-γ-CD/EC micelle, U-γ-CD/CA micelle, and U-γ-CD/CAB micelle, respectively.

As shown in Fig. 6, all profiles exhibit a steady continued-release pattern with certain amount of initial burst release. It is found that the prednisone acetate release from the micelles is fast in the first 6 h, that is, about 53%, 44%, 54% and 60% drug release from the mielles of U-β-CD/MC, U-γ-CD/EC, U-γ-CD/CA, and U-γ-CD/CAB, respectively. For the U-β-CD/MC micelle, the accumulated release rate was nearly 100% within 200 h. The sustained release of drug is observed up to 500 h in other three micelles. These results suggest that the cyclodextrin carbamate/cellulose derivative micelles could be used as a candidate for long time drug release.

4. Conclusions

In summary, cyclodextrin carbamate was prepared under solvent-free and catalyst-free conditions. The novel supramolecular polymer micelles based on cyclodextrin carbamate partly threaded on cellulose derivative were constructed in aqueous solution by one-pot self-assembly method. The spherical supramolecular polymer micelles with diameters ranged from 20 to 60 nm were obtained, showed lower CMC and sustained drug release behavior. The biocompatible and degradable supramolecular polymer micelles may be promising candidates for drug delivery.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.06.075.

References

Aguiar, J., Carpena, P., Molina-Bolívar, J. A., & Carnero Ruiz, C. (2003). On the determination of the critical micelle concentration by the pyrene 1:3 ratio method. *Journal of Colloid and Interface Science*, *258*, 116–122.

Anraku, Y., Kishimura, A., Yamasaki, Y., & Kataoka, K. (2013). Living unimodal growth of polyion complex vesicles via two-dimensional supramolecular polymerization. *Journal of the American Chemical Society*, *135*, 1423–1429.

Chang, C. Y., & Zhang, L. N. (2011). Cellulose-based hydrogels: Present status and application prospects. *Carbohydrate Polymers*, *84*, 40–53.

Chen, P., Liang, H. W., Lv, X. H., Zhu, H. Z., Yao, H. B., & Yu, S. H. (2011). Carbonaceous nanofiber membrane functionalized by beta-cyclodextrins for molecular filtration. *ACS Nano*, *5*, 5928–5935.

Chen, Y., Zhang, Y. M., & Liu, Y. (2010). Multidimensional nanoarchitectures based on cyclodextrins. *Chemical Communications*, *46*, 5622–5633.

Chen, Y. M. (2012). Shaped hairy polymer nanoobjects. *Macromolecules*, *45*, 2619–2631.

Cho, S. Y., & Allcock, H. R. (2009). Synthesis of adamantyl polyphosphazene-polystyrene block copolymers, and beta-cyclodextrin-adamantyl side group complexation. *Macromolecules*, *42*, 4484–4490.

Danquah, M., Fujiwara, T., & Mahato, R. I. (2010). Self-assembling methoxy-poly(ethylene glycol)-b-poly(carbonate-co-L-lactide) block copolymers for drug delivery. *Biomaterials*, *31*, 2358–2370.

Dong, H. Q., Li, Y. Y., Cai, S. J., Zhuo, R. X., Zhang, X. Z., & Liu, L. J. (2008). A facile one-pot construction of supramolecular polymer micelles from alpha-cyclodextrin and poly(epsilon-caprolactone). *Angewandte Chemie International Edition*, *47*, 5573–5576.

Dong, H. Q., Li, Y. Y., Wen, H. Y., Xu, M., Liu, L. J., Li, Z. Q., et al. (2011). Highly efficient drug delivery nanosystem via L-phenylalanine triggering based on supramolecular polymer micelles. *Macromolecular Rapid Communications*, *32*, 540–545.

Dong, T., Kai, W., Pan, P., Cao, A., & Inoue, Y. (2007). Effects of host–guest stoichiometry of α-cyclodextrin–aliphatic polyester inclusion complexes and molecular weight of guest polymer on the crystallization behavior of aliphatic polyesters. *Macromolecules*, *40*, 7244–7251.

Du, J. J., Guo, X., Tu, J. X., Xiao, L. Q., Jia, X. X., Liao, L. Q., et al. (2012). Biopolymer-based supramolecular micelles from beta-cyclodextrin and methylcellulose. *Carbohydrate Polymers*, *90*, 569–574.

Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A., Seiler, B. D., Shelton, M. C., et al. (2001). Advances in cellulose ester performance and application. *Progress in Polymer Science*, *26*, 1605–1688.

Guo, Y., Zhou, J. P., Wang, Y. C., Zhang, L. N., & Lin, X. Y. (2010). An efficient transformation of cellulose into cellulose carbamates assisted by microwave irradiation. *Cellulose*, *17*, 1115–1125.

Harada, A., Hashidzume, A., Yamaguchi, H., & Takashima, Y. (2009). Polymeric rotaxanes. *Chemical Reviews*, *109*, 5974–6023.

Harada, A., & Kamachi, M. (1990). Complex formation between poly(ethylene glycol) and α-cyclodextrin. *Macromolecules*, *23*, 2821–2823.

Huang, F. H., & Gibson, H. W. (2005). Polypseudorotaxanes and polyrotaxanes. *Progress in Polymer Science*, *30*, 982–1018.

Kalyanasundaram, K., & Thomas, J. K. (1977). Environmental effects on vibronic band intensities in pyrene monomer fluorescence and their application in studies of micellar systems. *Journal of the American Chemical Society*, *99*, 2039–2044.

Kang, H. L., Liu, R. G., & Huang, Y. (2013). Cellulose derivatives and graft copolymers as blocks for functional materials. *Polymer International*, *62*, 338–344.

Kawaguchi, Y., Nishiyama, T., Okada, M., Kamachi, M., & Harada, A. (2000). Complex formation of poly(epsilon-caprolactone) with cyclodextrins. *Macromolecules*, *33*, 4472–4477.

Kulkarni, A., DeFrees, K., Hyun, S. H., & Thompson, D. H. (2012). Pendant polymer: Amino-beta-cyclodextrin: siRNA guest: Host nanoparticles as efficient vectors for gene silencing. *Journal of the American Chemical Society*, *134*, 7596–7599.

Liao, X. J., Chen, G. S., Liu, X. X., Chen, W. X., Chen, F., & Jiang, M. (2010). Photoresponsive pseudopolyrotaxane hydrogels based on competition of host-guest interactions. *Angewandte Chemie International Edition*, *49*, 4409–4413.

Lu, J., Shin, I. D., Nojima, S., & Tonelli, A. E. (2000). Formation and characterization of the inclusion compounds between poly(epsilon-caprolactone)-poly(ethylene oxide)-poly(epsilon-caprolactone) triblock copolymer and alpha- and gamma-cyclodextrin. *Polymer*, *41*, 5871–5883.

Nada, A. A., Kamel, S., & El-Sakhawy, M. (2000). Thermal behaviour and infrared spectroscopy of cellulose carbamates. *Polymer Degradation and Stability*, *70*, 347–355.

Nepogodiev, S. A., & Stoddart, J. F. (1998). Cyclodextrin-based catenanes and rotaxanes. *Chemical Reviews*, *98*, 1959–1976.

Okumura, Y., & Ito, K. (2001). The polyrotaxane gel: A topological gel by figure-of-eight cross-links. *Advanced Materials*, *13*, 485–487.

Tamesue, S., Takashima, Y., Yamaguchi, H., Shinkai, S., & Harada, A. (2010). Photoswitchable supramolecular hydrogels formed by cyclodextrins and azobenzene polymers. *Angewandte Chemie International Edition*, *49*, 7461–7464.

Tao, W., Liu, Y., Jiang, B. B., Yu, S. R., Huang, W., Zhou, Y. F., et al. (2012). A linear-hyperbranched supramolecular amphiphile and its self-assembly into vesicles with great ductility. *Journal of the American Chemical Society*, *134*, 762–764.

Wang, D. Q., Tan, J. J., Kang, H. L., Ma, L., Jin, X., Liu, R. G., et al. (2011). Synthesis, self-assembly and drug release behaviors of pH-responsive copolymers ethyl cellulose-graft-PDEAEMA through ATRP. *Carbohydrate Polymers*, *84*, 195–202.

Wang, W., Li, Y., Sun, M., Zhou, C., Zhang, Y., Li, Y., et al. (2012). Colorimetric and fluorescent nanofibrous film as a chemosensor for Hg^{2+} in aqueous solution prepared by electrospinning and host–guest interaction. *Chemical Communications*, *48*, 6040–6042.

Wenz, G., Han, B. H., & Muller, A. (2006). Cyclodextrin rotaxanes and polyrotaxanes. *Chemical Reviews*, *106*, 782–817.

Xue, Y. N., Huang, Z. Z., Zhang, J. T., Liu, M., Zhang, M., Huang, S. W., et al. (2009). Synthesis and self-assembly of amphiphilic poly(acrylic acid-b-DL-lactide) to form micelles for pH-responsive drug delivery. *Polymer*, *50*, 3706–3713.

Yan, H., Zhu, L. L., Li, X., Kwok, A., Li, X., Agren, H., et al. (2013). Photothermal-responsive 2 rotaxanes. *RSC Advances*, *3*, 2341–2350.

Yan, Q., Xin, Y., Zhou, R., Yin, Y. W., & Yuan, J. Y. (2011). Light-controlled smart nanotubes based on the orthogonal assembly of two homopolymers. *Chemical Communications*, *47*, 9594–9596.

Yang, C., Ni, X. P., & Li, J. (2009). Synthesis of polyrotaxanes consisting of multiple alpha-cyclodextrin rings threaded on reverse pluronic PPO-PEO-PPO triblock copolymers based on block-selected inclusion complexation. *European Polymer Journal*, *45*, 1570–1579.

Yoshida, K., Shimomura, T., Ito, K., & Hayakawa, R. (1999). Inclusion complex formation of cyclodextrin and polyaniline. *Langmuir*, *15*, 910–913.

Yuen, F., & Tam, K. C. (2013). alpha-cyclodextrin assisted self-assembly of poly(ethylene glycol)-block-poly(N-isopropylacrylamide) in aqueous media. *Journal of Applied Polymer Science*, *127*, 4785–4794.

Zhao, S. P., Zhang, L. M., & Ma, D. (2006). Supramolecular hydrogels induced rapidly by inclusion complexation of poly(epsilon-caprolactone)-poly(ethylene glycol)-poly(epsilon-caprolactone) block copolymers with alpha-cyclodextrin in aqueous solutions. *Journal of Physical Chemistry B*, *110*, 12225–12229.

Zhu, Y. Q., Liu, L., & Du, J. Z. (2013). Probing into homopolymer self-assembly: How does hydrogen bonding influence morphology? *Macromolecules*, *46*, 194–203.