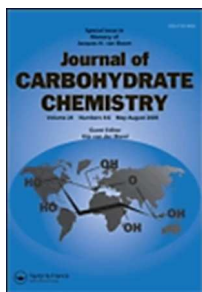


## Self-Assembling Properties of 6-0- and 6-0-Alkylsucrose Mixtures Having Different Chain Lengths Under Aqueous Conditions

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## Self-Assembling Properties of 6-*O*- and 6'-*O*-Alkylsucroses Mixtures Having Different Chain Lengths under Aqueous Conditions

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In this **study**, we report the self-assembling properties of the 6-*O*- and 6'-*O*-alkylsucroses mixtures with different chain lengths, that is, octyl, decyl, dodecyl, and tetradecyl, under aqueous conditions, **and which** were further compared with those of the 6-*O*- and 6'-*O*-hexadecylsucroses mixture reported in our previous publication. The materials were synthesized from sucrose **via five reaction steps**. The results of scanning and transmission electron microscopes, powder X-ray diffraction, and dynamic light scattering measurements indicated that the self-assembling properties of the former three derivatives were completely different from those of the 6-*O*- and 6'-*O*-hexadecylsucroses mixture. The present three derivatives primary formed lamellar planes, which further induced the formation of vesicle-type particles under aqueous conditions, whereas the previous derivative primary formed spherical micelles in water, which further assembled according to face-centered cubic organization by drying process from the aqueous dispersion. It was also found that the 6-*O*- and 6'-*O*-tetradecylsucroses mixture showed concentration-induced micelle-lamellar transition behavior in an aqueous dispersion. Furthermore, the series of our studies on the self-assemblies of 6-*O*- and 6'-*O*-alkylsucroses indicated that the mixing of a stereoisomer, 6'-*O*-hexadecylsucrose, with 6-*O*-hexadecylsucrose induced the different self-assembling property from that of a sole 6-*O*-hexadecylsucrose, but this effect was not appeared in the self-assembling property of the

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5 6-*O*- and 6'-*O*-octylsucroses mixture.  
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11 **Keywords** Sucrose; Monoalkyl ether; Self-assembly; Micelle; Lamellar  
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## 28 **INTRODUCTION**

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31 Amphiphilic molecules, so-called amphiphiles, possess antagonistic hydrophilic and hydrophobic moieties in  
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33 the same molecule. In aqueous media, such molecules self-assemble or -organize into diverse aggregate  
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35 morphologies, such as spherical micelles, cylindrical micelles, spherical vesicles, planer bilayers, and tubes,  
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37 depending on the molecular shape and solution conditions.<sup>[1]</sup> Because glycolipids, which are natural amphiphiles  
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39 composed of carbohydrates as a hydrophilic part, exhibit important in vivo functions in living systems,<sup>[2]</sup> synthetic  
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41 carbohydrate-based amphiphiles have extensively been studied to exhibit a large variety of self-assembling  
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43 morphologies.<sup>[1]</sup>  
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51 In the practical application field, synthetic carbohydrate-based amphiphiles have specifically been employed as  
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53 additives in various food industries in the form of emulsifiers.<sup>[3]</sup> One of the most effective food additives,  
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55 practically employed, is the sucrose fatty acid ester, which is composed of a sucrose residue as a hydrophilic part  
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5 and long-alkyl fatty acid moieties as a hydrophobic part.<sup>[4]</sup> The self-assembling properties of the sucrose fatty acid  
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8 esters changed depending on the lengths and types of fatty acid chains and have been investigated extensively.<sup>[5]</sup>  
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10 In comparison, self-assembling studies of sucrose ether amphiphiles carrying long-alkyl chains attached by ether  
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12 linkages to the sucrose residue have been less reported. As one of the examples, the effect of molecular shape on  
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14 the liquid crystal properties of mono-*O*-(2-hydroxydodecyl)sucroses was reported.<sup>[6]</sup> In the previous paper, we  
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16 reported the following self-assembling process of a mixture of 6-*O*- and 6'-*O*-hexadecylsucroses (**C16-mixture**)  
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18 under aqueous conditions.<sup>[7]</sup> The mixture primary formed spherical micelles with a diameter of approximately 5-7  
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20 nm in water, which hierarchically organized according to face-centered cubic (FCC) structure during drying  
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22 process from the aqueous dispersion to construct nanoparticles with a diameter of approximately 50 nm. Moreover,  
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24 several numbers of the nanoparticles further assembled to form larger aggregates. In the following investigation,  
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26 furthermore, we could synthesize a sole 6-*O*-hexadecylsucrose, and thus, evaluated its self-assembling property  
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28 under aqueous conditions.<sup>[8]</sup> Consequently, it was found that the self-assembling process of the sole molecule was  
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30 completely different from that of its mixture with the regioisomer, 6'-*O*-hexadecylsucrose, that is, **C16-mixture**,  
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32 in which the sole molecule showed hierarchical self-assembling process based on the primary formation of  
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34 lamellar planes, leading to vesicle-type particles. It was also revealed that the other 6-*O*-alkylsucrose with a  
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36 different chain length, that is, 6-*O*-octylsucrose, was found to show the same self-assembling process as that of  
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38 6-*O*-hexadecylsucrose. The above results indicated that the self-assembling properties of monoalkylsucroses are  
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40 different depending on the subtle change of their molecular shapes.  
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57 In the present study, on the basis of the above viewpoints, we synthesized the series of the 6-*O*- and  
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5 6'-O-alkylsucroses mixtures having different chain lengths, that is, octyl, decyl, dodecyl, and tetradecyl  
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8 (C8-mixture, C10-mixture, C12-mixture, and C14-mixture, respectively) and evaluated their self-assembling  
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10 properties under aqueous conditions, which were further compared with those of C16-mixture revealed in our  
11  
12 previous study.<sup>[7]</sup> Consequently, the former three derivatives showed the different self-assembling properties from  
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14 those of C16-mixture, but same as that of 6-O-hexadecylsucrose as well as 6-O-octylsucrose. Interestingly,  
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16 C14-mixture exhibited the different self-assembling properties depending on the concentrations of its aqueous  
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18 dispersions.  
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## 28 **RESULT AND DISCUSSION**

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31 The series of the 6-O- and 6'-O-alkylsucroses mixtures were synthesized from sucrose according to the same  
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33 procedure as that described in our previous paper (Scheme 1).<sup>[7]</sup> Thus, the common intermediate **3** having a  
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35 hydroxy group at the 6- or 6'-position was first prepared by the successive tritylation at the 6- or 6'-position of  
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37 sucrose, benzylation of the other hydroxy groups, and detritylation. Then, the etherification of **3** with the  
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39 corresponding alkyl bromides was performed in the presence of sodium hydride in DMF at elevated temperatures.  
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41 The following debenylation of the products was conducted by catalytic hydrogenation under the appropriate  
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43 conditions to give C8-mixture, C10-mixture, C12-mixture, and C14-mixture. The structures of the materials  
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45 were confirmed by the <sup>1</sup>H NMR and MALDI-TOF MS measurements (see experimental section). The molar ratios  
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47 of 6-ether to 6'-ether in the products, which were calculated from the integrated ratios of two H1 signals of the  
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49 glucose residues, were almost 1:1 or even higher as the values are given in the experimental section because of the  
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5 higher reactivity of the 6-position than the 6'-position.  
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8 Then, the resulting products were subjected to the following investigations of their self-assembly properties  
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10 under aqueous conditions. In the scanning electron microscope (SEM) images of the samples on aluminum plates  
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12 (Fig. 1), which were prepared by drying dispersions of the products in water ( $1 \times 10^{-5}$  mol/L), particle-like  
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14 nanoaggregates were seen. The average diameters of the particles from the **C8-mixture**, **C10-mixture**,  
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16 **C12-mixture**, and **C14-mixture** samples were 169, 104, 173, and 156 nm, respectively (the values of the standard  
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18 deviations are shown in Table 1). The values and morphologies were much different from those of the  
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20 **C16-mixture** sample because nanoparticles with the average diameter of ~50 nm by hierarchically organization  
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22 according to the FCC structure and larger aggregates, which were formed by further assembly of the nanoparticles  
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24 probably due to their greater density, were observed in the SEM image of the **C16-mixture** sample (Fig. 1(e),  
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26 Table 1). Moreover, the standard deviation in the diameters of **C16-mixture** was much smaller than that in the  
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28 diameters of the other particles (4.34 and 16 - 45, respectively). To further confirm the hierarchical structures of  
29  
30 the nanoparticles, the transmission electron microscope (TEM) measurement of the selected samples was  
31  
32 performed. Dispersions of **C8-mixture** and **C16-mixture** in water ( $1.0 \times 10^{-5}$  mol/L) were placed on carbon  
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34 film-coated grids. After completing the negative-staining technique, the TEM samples were prepared by drying  
35  
36 the preparative materials. The TEM image of the **C8-mixture** sample (Fig. 2(a)) exhibited vesicle-type particles  
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38 with diameters of approximately 100 – 150 nm, whereas in the TEM image of the **C16-mixture** sample (Fig. 2(b)),  
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40 some particles with the diameters smaller than 50 nm were seen, which did not exhibit the vesicle-like  
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42 morphology. The above SEM and TEM results indicated that the self-assembling processes of the present  
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5 derivatives under aqueous conditions were completely different from those of **C16-mixture** under the same  
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7 conditions.  
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10 To confirm the self-assembling processes of these derivatives in drying state from aqueous dispersions in even  
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12 greater detail, the powder X-ray diffraction (XRD) measurement was conducted. Fig. 3 shows the XRD profiles of  
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14 the **C8-mixture**, **C10-mixture**, **C12-mixture**, **C14-mixture**, and **C16-mixture** samples, which were prepared by  
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16 drying their aqueous dispersions ( $1.0 \times 10^{-3}$  mol/L). As reported in our previous paper,<sup>[7]</sup> the XRD profile of  
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18 **C16-mixture** exhibited diffraction peaks ascribable to the (111), (200), (311/222), (400), and (600) Bragg  
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20 reflections of the FCC structure based on the primary formation of spherical micelles. In the XRD profiles of the  
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22 other derivatives, on the other hand, diffraction peaks due to (001) and (002) Bragg reflections of the lamellar  
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24 patterns were observed. From the XRD patterns, it was found that the widths of each lamellar layer increased with  
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26 an increase in the alkyl chain lengths and were calculated to be 3.00 nm for **C8-mixture**, 3.37 nm for  
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28 **C10-mixture**, 3.76 nm for **C12-mixture**, and 4.02 nm for **C14-mixture**. These XRD results of the present four  
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30 samples suggested that the lamellar planes probably with alternating hydrophilic sucrose and hydrophobic alkyl  
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32 layers were primary formed, which further constructed the vesicle-type nanoparticles with the 100 - 150 nm  
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34 diameters during drying process from the aqueous dispersions as observed in the SEM and TEM images (Fig.  
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36 **5(a)**).  
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51 To evaluate the self-assembling properties of the above materials in aqueous dispersions, then, the dynamic  
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53 light scattering (DLS) measurement was performed ( $1.0 \times 10^{-3}$  mol/L). In our previous paper, we reported the  
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55 observation of a monomodal profile with the average diameter of ca. 7 nm corresponding to a spherical micelle  
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5 (Fig. 5(b)) in the DLS profile of the aqueous dispersion of **C16-mixture** as shown in Fig. 4(e).<sup>[7]</sup> On the other  
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8 hand, the DLS results of the aqueous dispersions of **C8-mixture**, **C10-mixture**, and **C12-mixture** showed the  
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10 formation of the larger aggregates with the average diameters of 106.4, 126.5, and 102.8 nm, respectively (Figs.  
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13 4(a)-(c)), which probably corresponded to the vesicle-like particles formed from the lamellar planes (Fig 5(a)).  
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16 The self-assembling processes of these samples were same as those of the sole 6-*O*-octylsucrose and  
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18 6-*O*-tetradecylsucrose.<sup>[8]</sup> On the other hand, the DLS profile of the aqueous dispersion of **C14-mixture** in the  
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20 same concentration showed the smaller particles with the average diameter of 6.8 nm (Fig. 4(d)) as similar as that  
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22 of **C16-mixture**. This result suggested that **C14-mixture** formed the spherical micelles in this concentration in  
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24 water, but that was not consistent with the self-assembling structure in solid state as observed in the XRD result,  
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26 which indicated the formation of the lamellar planes. Interestingly, the average diameter increased to ~82 nm  
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28 when the DLS measurement of the aqueous dispersion of **C14-mixture** was conducted under the higher  
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30 concentration conditions ( $1.0 \times 10^{-2}$  mol/L) (Fig. 4(d')). It was further confirmed by the DLS measurement that  
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32 the diameters of the particles in the aqueous dispersions of **C14-mixture** were reversibly changed as Figs. 4(d)  
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34 and 4(d') depending on the concentrations. These results suggested that **C14-mixture** showed the  
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36 concentration-induced micelle-lamellar transition behavior in the aqueous dispersion as shown in Fig. 5.<sup>[9]</sup>  
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39 Therefore, it was reasonably explained that the XRD profile of the **C14-mixture** sample in solid state prepared by  
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41 drying the aqueous dispersion exhibited the lamellar pattern. Furthermore, the comprehensive results of our  
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43 present and previous studies suggested that the mixing of the stereoisomer, 6'-*O*-tetradecylsucrose, with  
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45 6-*O*-tetradecylsucrose, that is, **C16-mixture**, induced the different self-assembling property from that of the sole  
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5 6-*O*-tetradecylsucrose, but the mixing did not affect the self-assembling property of **C8-mixture**.<sup>[7,8]</sup> The reason  
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8 for the difference in the self-assembling processes of the aforementioned derivatives is not yet clear, but it is  
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10 obviously suggested that the subtle difference of their chemical structures strongly affects their self-assembling  
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12 properties under aqueous conditions. More detailed studies using methods based on calculations that consider  
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14 factors such as critical packing parameters are now in progress to further investigate the reasons for the difference  
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17 in their self-assembling processes.  
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## 25 **CONCLUSION**

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28 This study investigated the comparison of the characteristic self-assembling processes in the five 6-*O*- and  
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30 6'-*O*-alkylsucroses mixtures (**C8-mixture**, **C10-mixture**, **C12-mixture**, **C14-mixture**, and **C16-mixture**) with  
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32 different chain lengths under aqueous conditions. The former four derivatives were presently synthesized from  
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34 sucrose via the five reaction steps, whereas the latter one has already been synthesized in our previous study.<sup>[7]</sup>  
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36  
37 The self-assembling properties of the materials under aqueous conditions were evaluated by the SEM, TEM, XRD,  
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39 and DLS measurements. Consequently, the former three materials (**C8-mixture**, **C10-mixture**, and **C12-mixture**)  
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41  
42 primary formed the lamellar-like planes in water, which further constructed the vesicle-type particles (Fig. 5(a)),  
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45 whereas, as previously reported by us,<sup>[7]</sup> **C16-mixture** formed the spherical micelles in water, which then  
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48 assembled according to the FCC organization during the drying process from the aqueous dispersion to construct  
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51 the nanoparticles with size of approximately 50 nm (Fig. 5(b)). Interestingly, **C14-mixture** showed the  
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54 concentration-induced micelle-lamellar transition behavior in the aqueous dispersion as shown in Fig. 5, probably  
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5 due to the intermediary nature between **C12-mixture** and **C16-mixture**. Taking the previous results in addition to  
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8 the present results into consideration as summarized in Table 1, furthermore, it was also confirmed that the mixing  
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11 of the stereoisomer, 6'-*O*-tetradecylsucrose, with 6-*O*-tetradecylsucrose induced the different self-assembling  
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14 property from that of the sole 6-*O*-tetradecylsucrose, but the mixing effect was not observed in the self-assembling  
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16 property of **C8-mixture**.<sup>[7,8]</sup>  
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## 22 **EXPERIMENTAL**

### 23 **General**

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28 The common intermediate **3** and **C16-mixture** were prepared from sucrose according to the literature procedure  
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30 reported by us.<sup>[7]</sup> <sup>1</sup>H NMR spectra were recorded on a JEOL ECX400 spectrometer. MALDI-TOF MS  
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32 measurements were carried out by using SHIMADZU Voyager Biospectrometry Workstation Ver.5.1 with  
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34 2,5-dihydroxybenzoic acid as matrix containing 0.05 % trifluoroacetic acid under positive ion mode. SEM images  
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36 were obtained using Hitachi S-4100H electron microscope. The average particle diameters and standard  
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38 deviations were calculated on the basis of 50 objects for each SEM image. TEM measurements were operated  
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40 using Jeol JEM-3010 under 200 kV. XRD measurements were conducted using a PANalytical X'Pert Pro MPD  
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42 with Ni-filtered CuK $\alpha$  radiation ( $\lambda = 0.15418$  nm). DLS measurement was performed on a Zetasizer Nano ZS  
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44 (Malvern Instruments).  
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### 53 **Synthesis of 6-*O*-octyl- and 6-*O*-octylsucroses mixture (C8-mixture)**

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56 Under argon, to a dispersion of NaH (0.105 g, 4.36 mmol) in DMF (5.8 mL) was added a solution of **3** (0.556 g,  
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0.582 mmol) in DMF (11.6 mL) at room temperature and the mixture was stirred at that temperature for 30 min. After a solution of tetrabutylammonium bromide (small amount) in DMF (2.0 mL) and 1-bromooctane (0.36 mL, 2.04 mmol) were added to the mixture, the etherification was conducted at 80 °C for 20 h. The reaction was stopped by addition of methanol to the reaction mixture. After the resulting mixture was concentrated and diluted with chloroform, the solution was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The residue was subjected to column chromatography on silica gel (eluent; ethyl acetate : hexane = 1 : 50 (v/v)) to give 1',2,3,3',4,4,6'-hepta-*O*-benzyl-6-*O*-octyl- and 1',2,3,3',4,4,6-hepta-*O*-benzyl-6'-*O*-octylsucroses (**4-C8**, 0.101 g, 0.0928 mmol) in 15.9 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.86 (t, 3H, CH<sub>3</sub>, *J* = 4.8 Hz), 1.22 – 1.25 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20 – 4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35 – 4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, *J* = 5.2 and 3.6 Hz), 7.22 – 7.34 (m, 35H, aromatics).

To a solution of **4-C8** (0.101 g, 0.0928 mmol) in a mixed solvent of butanol, methanol, and water (2.14 mL, 10 : 1 : 0.25 (v/v/v)) was added 10% palladium on carbon (0.02 g) and the mixture was stirred at room temperature for 3.5 h under hydrogen atmosphere. After the reaction mixture was filtered and the filtrate was evaporated, the residue was subjected to column chromatography on silica gel (eluent; chloroform : methanol = 10 : 1) to give 6-*O*- and 6'-*O*-octylsucroses (**C8-mixture**, 0.023 g, 0.051 mmol, 6-ether : 6'-ether = 1:1) in 55.0 % yield. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 0.86 (t, 3H, CH<sub>3</sub>, *J* = 4.8 Hz), δ 1.30 - 1.33 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-CH<sub>3</sub>), 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21 - 4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H, H-1, *J* = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>20</sub>H<sub>38</sub>O<sub>11</sub>]<sup>+</sup>Na<sup>+</sup>: *m/z* 477.2312. Found: *m/z* 477.4204.

### Synthesis of 6-*O*-decyl- and 6-*O*-decylsucroses mixture (**C10-mixture**)

In the same way as **4-C8**, **4-C10** was prepared by the reaction of **3** with 3.5 equivalents of 1-bromodecane at 80 °C for 20 h in 51.2% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.86 (t, 3H, CH<sub>3</sub>, *J* = 6.2 Hz), 1.22 – 1.25 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20 – 4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35 – 4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, *J* = 4.8 and 4.0 Hz), 7.22 – 7.34 (m, 35H, aromatics).

Then, synthesis of **C10-mixture** was carried out in the same way as **C8-mixture** from **4-C10** in 4.5% yield, (6-ether : 6'-ether = 1:1). <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 0.87 (t, 3H, CH<sub>3</sub>, *J* = 6.2 Hz), δ 1.30 - 1.33 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-CH<sub>3</sub>), 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21 - 4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H, H-1, *J* = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>22</sub>H<sub>42</sub>O<sub>11</sub>Na]<sup>+</sup>: *m/z* 505.2625. Found: *m/z* 505.3256.

#### Synthesis of 6-*O*-dodecyl- and 6-*O*-dodecylsucuroses mixture (**C12-mixture**)

In the same way as **4-C8**, **4-C12** was prepared by the reaction of **3** with 3.5 equivalents of 1-bromododecane at 80 °C for 20 h in 39.4% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.87 (t, 3H, CH<sub>3</sub>, *J* = 6.8 Hz), 1.22 – 1.25 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20 – 4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35 – 4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, *J* = 4.8 and 3.6 Hz), 7.22 – 7.34 (m, 35H, aromatics).

Then, synthesis of **C12-mixture** was carried out in the same way as **C8-mixture** from **4-C12** in 7.28% yield (6-ether : 6'-ether = 5:2). <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 0.89 (t, 3H, CH<sub>3</sub>, *J* = 7.2 Hz), δ 1.30 - 1.33 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>), 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21 - 4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H, H-1, *J* = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>24</sub>H<sub>46</sub>O<sub>11</sub>Na]<sup>+</sup>: *m/z* 533.2938. Found: *m/z* 533.4521.

#### Synthesis of 6-*O*-tetradecyl- and 6-*O*-tetradecylsucuroses mixture (**C14-mixture**)

In the same way as **4-C8**, **4-C14** was prepared by the reaction of **3** with 3.5 equivalents of 1-bromotetradecane

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5 at 80 °C for 20 h in 26.5% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88 (t, 3H, CH<sub>3</sub>, *J* = 6.8 Hz), 1.22 – 1.25 (m, 22H,  
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8 -(CH<sub>2</sub>)<sub>11</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20 – 4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35 –  
9  
10 4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, *J* = 4.8 and 4.0 Hz), 7.22 – 7.34 (m, 35H, aromatics).

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13 Then, synthesis of **C14-mixture** was carried out in the same way as **C8-mixture** from **4-C14** in 6.19% yield  
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15 (6-ether : 6'-ether = 5:3). <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 0.89 (t, 3H, CH<sub>3</sub>, *J* = 7.2 Hz), δ 1.30 - 1.33 (m, 22H, -(CH<sub>2</sub>)<sub>11</sub>-CH<sub>3</sub>),  
16  
17 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21 - 4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H,  
18  
19 H-1, *J* = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>26</sub>H<sub>50</sub>O<sub>11</sub>Na]<sup>+</sup>: *m/z* 561.3251. Found: *m/z* 561.4976.  
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#### 24 25 **Preparation of samples for SEM measurement**

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27  
28 A dispersion of 6-*O*- and 6'-*O*-alkylsucroses mixture (1.0 x 10<sup>-5</sup> mol/L) was placed on an aluminum plate and it  
29  
30 was left standing under ambient atmosphere until water was evaporated. Then, the resulting solid sample was  
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32 subjected to the measurement.  
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#### 35 36 **Preparation of samples for TEM measurement**

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39 A dispersion of 6-*O*- and 6'-*O*-alkylsucroses mixture (1.0 x 10<sup>-5</sup> mol/L) was placed on carbon film-coated  
40  
41 copper grid. The negative-staining technique was used for TEM sample preparation. Then, the preparative  
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43 material was left standing under ambient atmosphere until water was evaporated. Then, the resulting solid sample  
44  
45 was subjected to the measurement.  
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#### 50 51 **Preparation of samples for XRD measurement**

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54 A dispersion of 6-*O*- and 6'-*O*-alkylsucroses mixture (1.0 x 10<sup>-3</sup> mol/L) was placed on a sample plate and it was  
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56 left standing under ambient atmosphere until water was evaporated. Then, the resulting solid sample was  
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5 subjected to the measurement.  
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### Scheme and Figure Captions

**Scheme 1.** Synthesis of 6-*O*- and 6'-*O*-alkylsucroses mixtures with different chain lengths (**C8-mixture**, **C10-mixture**, **C12-mixture**, and **C14-mixture**) from sucrose.

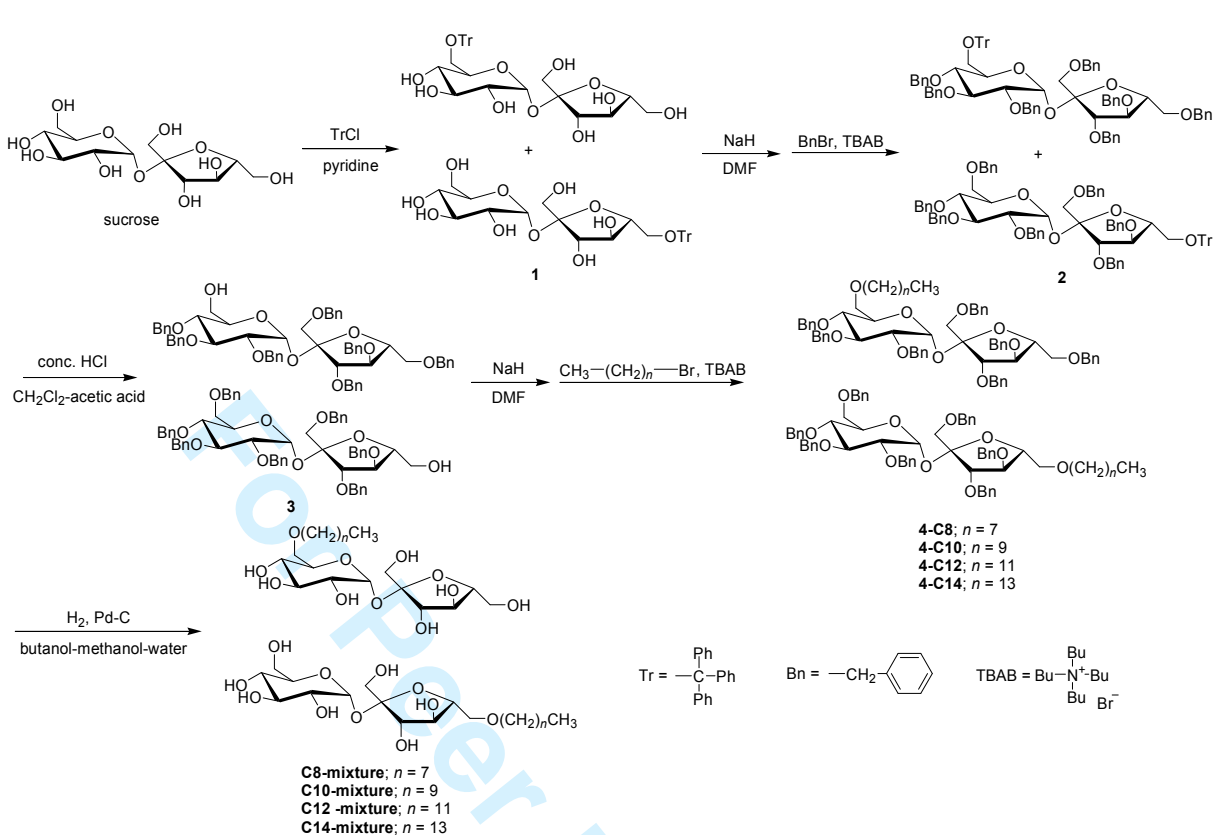
**Figure 1.** SEM images of the samples prepared from dispersions of (a) **C8-mixture**, (b) **C10-mixture**, (c) **C12-mixture**, (d) **C14-mixture**, and (e) **C16-mixture** in water ( $1.0 \times 10^{-5}$  mol/L).

**Figure 2.** TEM images of the samples prepared from dispersions of (a) **C8-mixture** and (b) **C16-mixture** in water ( $1.0 \times 10^{-5}$  mol/L).

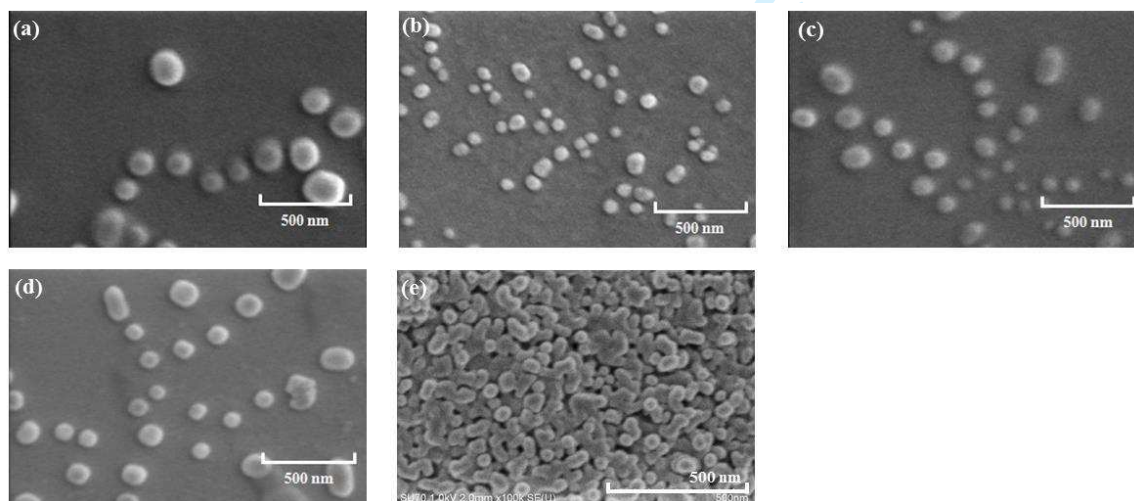
**Figure 3.** XRD profiles of the samples prepared from dispersions of (a) **C8-mixture**, (b) **C10-mixture**, (c) **C12-mixture**, (d) **C14-mixture**, and (e) **C16-mixture** in water ( $1.0 \times 10^{-3}$  mol/L).

**Figure 4.** DLS profiles of (a) **C8-mixture**, (b) **C10-mixture**, (c) **C12-mixture**, (d) **C14-mixture**, and (e) **C16-mixture** in water ( $1.0 \times 10^{-3}$  mol/L) and (d') **C14-mixture** in water ( $1.0 \times 10^{-2}$  mol/L).

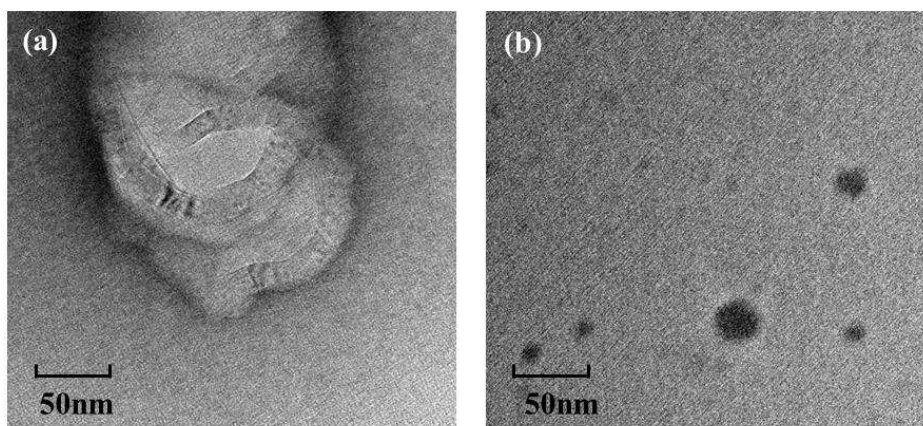
**Figure 5.** Plausible self-assembling processes of (a) **C8-mixture**, **C10-mixture**, **C12-mixture**, and **C14-mixture** (higher concentration) and (b) **C14-mixture** (lower concentration) and **C16-mixture** under aqueous conditions.



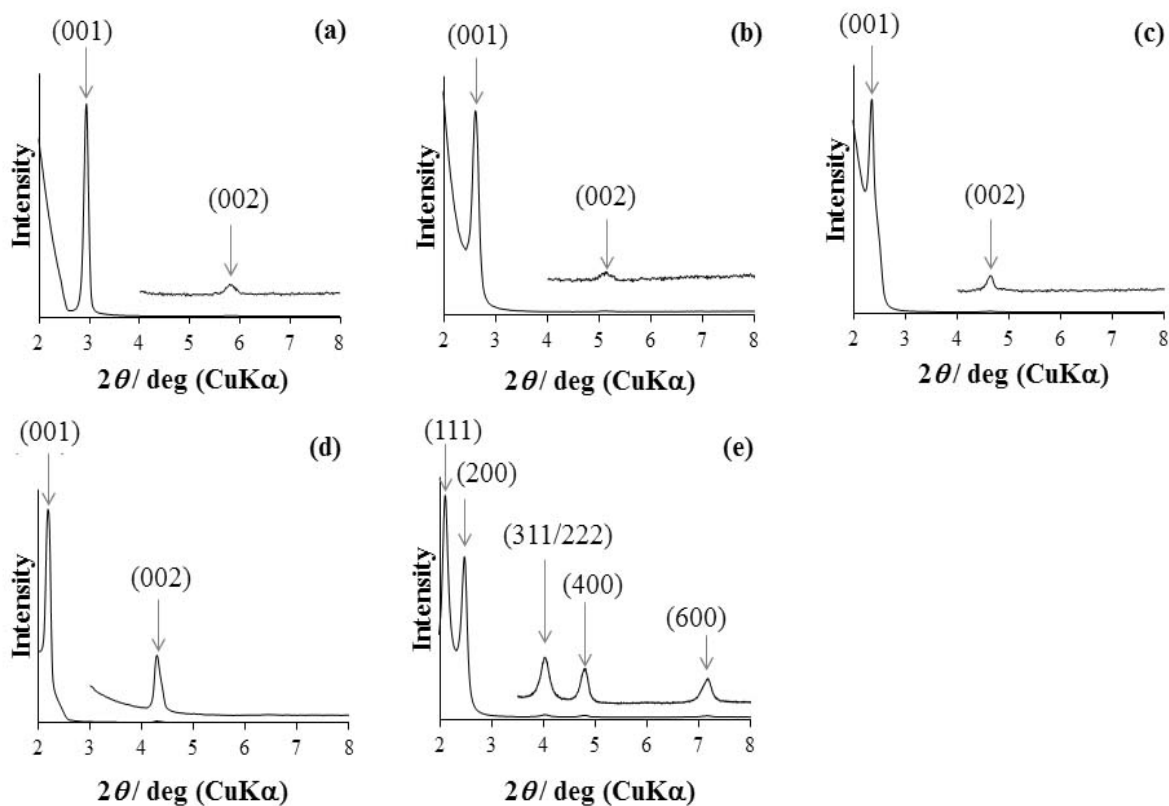
29 **Scheme 1.** Synthesis of 6-*O*- and 6'-*O*-alkylsucroses mixtures with different chain lengths (**C8-mixture**,  
30 **C10-mixture**, **C12-mixture**, and **C14-mixture**) from sucrose.



55 **Figure 1.** SEM images of the samples prepared from dispersions of (a) **C8-mixture**, (b) **C10-mixture**, (c)  
56 **C12-mixture**, (d) **C14-mixture**, and (e) **C16-mixture** in water ( $1.0 \times 10^{-5}$  mol/L).



**Figure 2.** TEM images of the samples prepared from dispersions of (a) **C8-mixture** and (b) **C16-mixture** in water ( $1.0 \times 10^{-5}$  mol/L).



**Figure 3.** XRD profiles of the samples prepared from dispersions of (a) **C8-mixture**, (b) **C10-mixture**, (c) **C12-mixture**, (d) **C14-mixture**, and (e) **C16-mixture** in water ( $1.0 \times 10^{-3}$  mol/L).

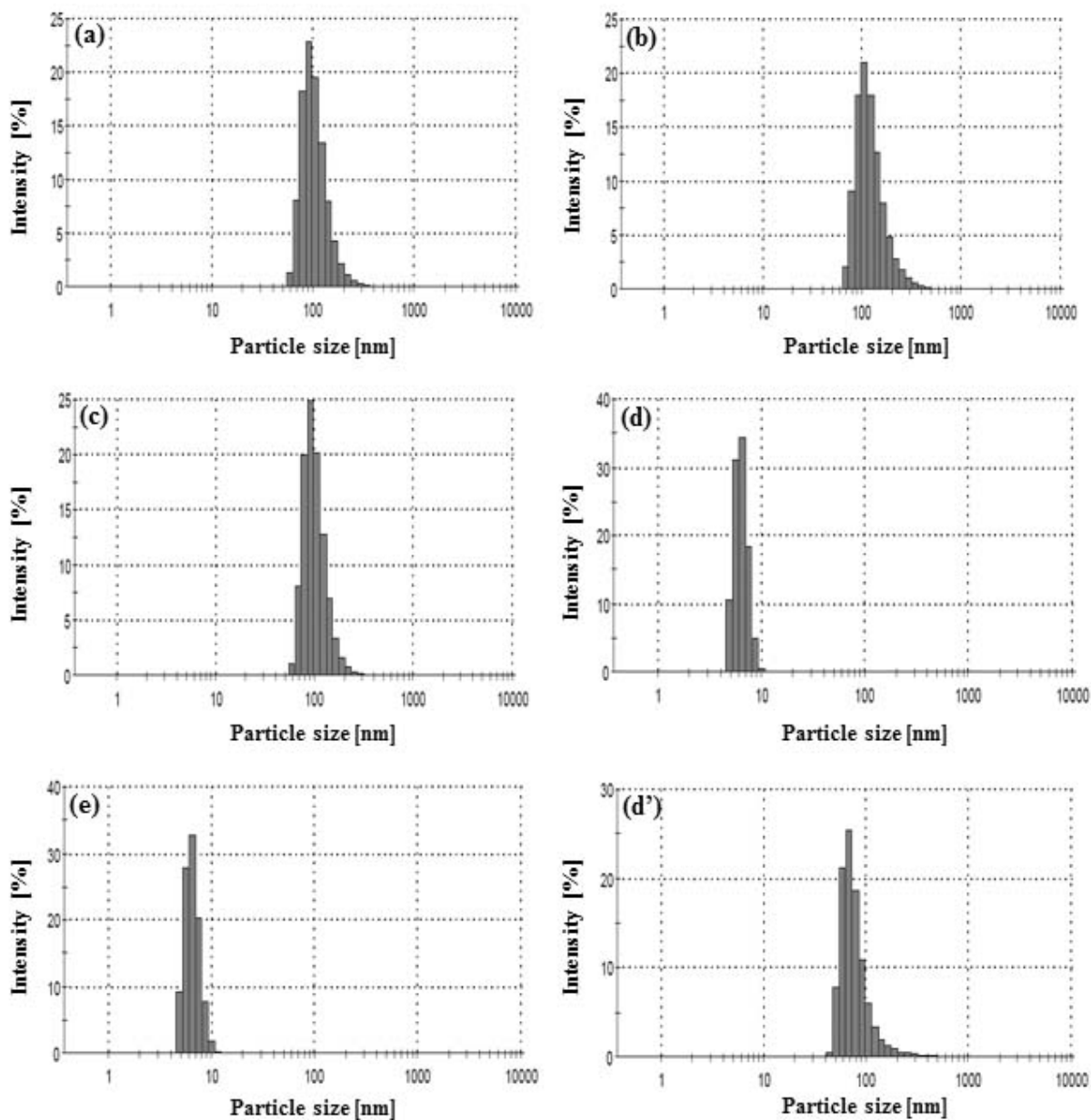
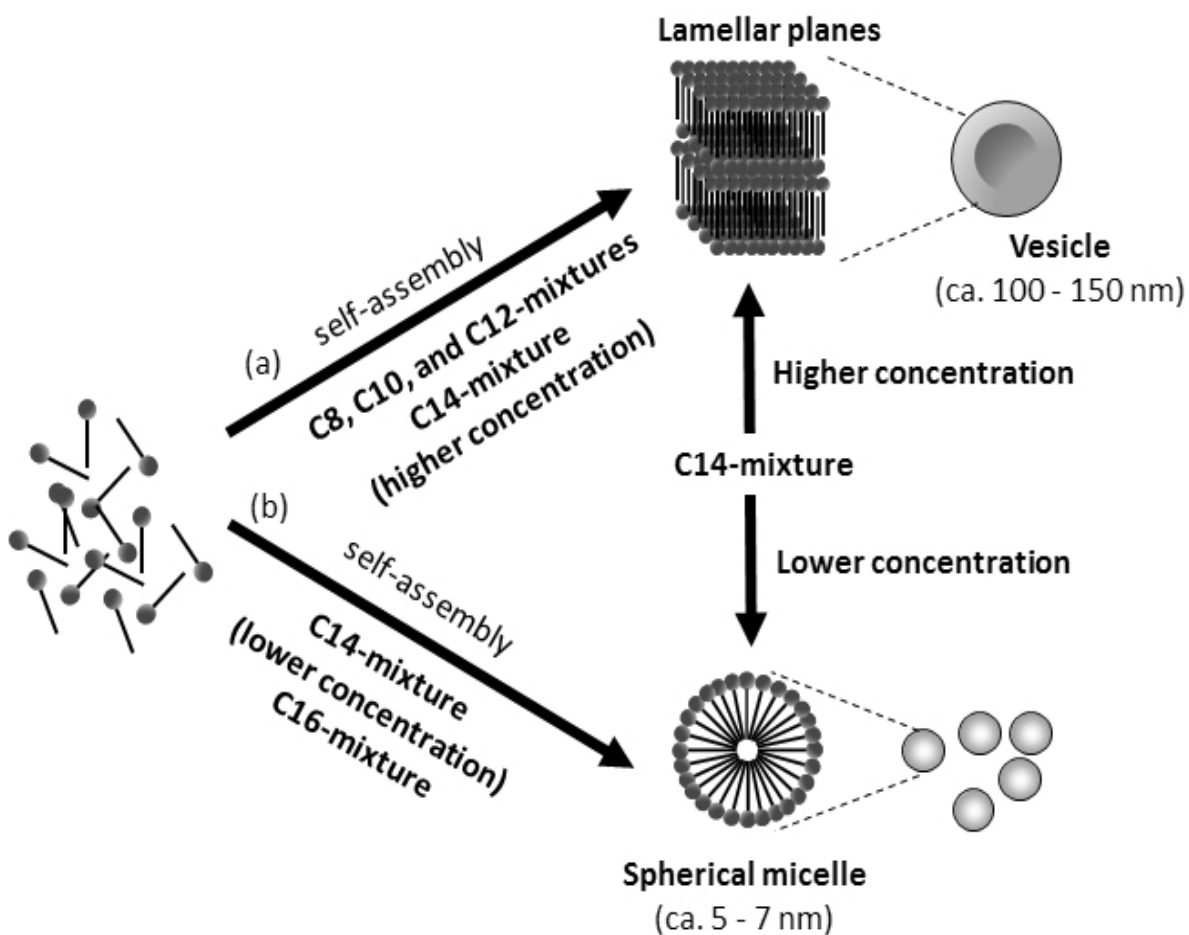


Figure 4. DLS profiles of (a) C8-mixture, (b) C10-mixture, (c) C12-mixture, (d) C14-mixture, and (e) C16-mixture in water ( $1.0 \times 10^{-3}$  mol/L) and (d') C14-mixture in water ( $1.0 \times 10^{-2}$  mol/L).



**Figure 5.** Plausible self-assembling processes of (a) C8-mixture, C10-mixture, C12-mixture, and C14-mixture (higher concentration) and (b) C14-mixture (lower concentration) and C16-mixture under aqueous conditions.

**Table 1:** SEM, DLS, and XRD results of sucrose ethers

Sample	SEM results		Average diameters (nm) by DLS results ( $1.0 \times 10^{-3}$ mol/L)	XRD results
	Average diameter (nm)	Standard deviation		
<b>C8-mixture</b>	169	44.8	106.4	lamellar
6-O-octylsucrose <sup>a</sup>	117	14.4	105.9	lamellar
			( $1.0 \times 10^{-5}$ mol/L)	
<b>C10-mixture</b>	104	16.3	126.5	lamellar
<b>C12-mixture</b>	173	26.2	102.8	lamellar
<b>C14-mixture</b>	156	22.3	6.8	lamellar
			82.0	
			( $1.0 \times 10^{-2}$ mol/L)	
<b>C16-mixture<sup>b</sup></b>	50	4.34	7.1	micelle
			( $1.0 \times 10^{-5}$ mol/L)	
<b>6-O-hexadecylsucrose<sup>a</sup></b>	51	12.8	99.8	lamellar
			( $1.0 \times 10^{-5}$ mol/L)	

<sup>a</sup> Reference 8. <sup>b</sup> Reference 7.