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Synthesis and aqueous solution properties of PAMAM dendron surfactants bearing a quaternary ammonium focal group and sugar terminal groups

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ABSTRACT

Poly(amidoamine) (PAMAM) dendron surfactants bearing a focal quaternary alkyldimethylammonium group and terminal sugar groups ($C_m\text{qb-GnLac}$; $m = 12, 18, 22$; $n = 0, 1$) have been synthesized. Solution properties of these dendron surfactants were investigated by means of static surface tension, electric conductivity, fluorescence probing with pyrene, dynamic light scattering (DLS) and static light scattering (SLS). In the surface tension profiles all $C_m\text{qb-GnLac}$ systems indicate a clear break point corresponding to the critical micelle concentration (cmc). The cmc decreases with increasing length of alkyl chain, from 8.2×10^{-3} (C_{12}) to 4.5×10^{-6} mol dm⁻³ (C_{22}) for G0Lac, from 1.0×10^{-2} (C_{12}) to 3.7×10^{-5} mol dm⁻³ (C_{22}) for G1Lac systems. Unlike conventional cationic surfactants, the surface tension at cmc (γ_{cmc}) significantly increases with increasing alkyl chain length, associated with a slight increase in the molecular occupied area. Degree of counter ion (Br^-) binding to the micelles is found to be very low due to an effective charge shielding by bulky non-ionic headgroups. In all $C_m\text{qb-GnLac}$ systems the micellar size decreases above a certain concentration. In the higher concentration regime, formation of micelles with a very small number of (at most a few) molecules is suggested from DLS data.

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1. Introduction

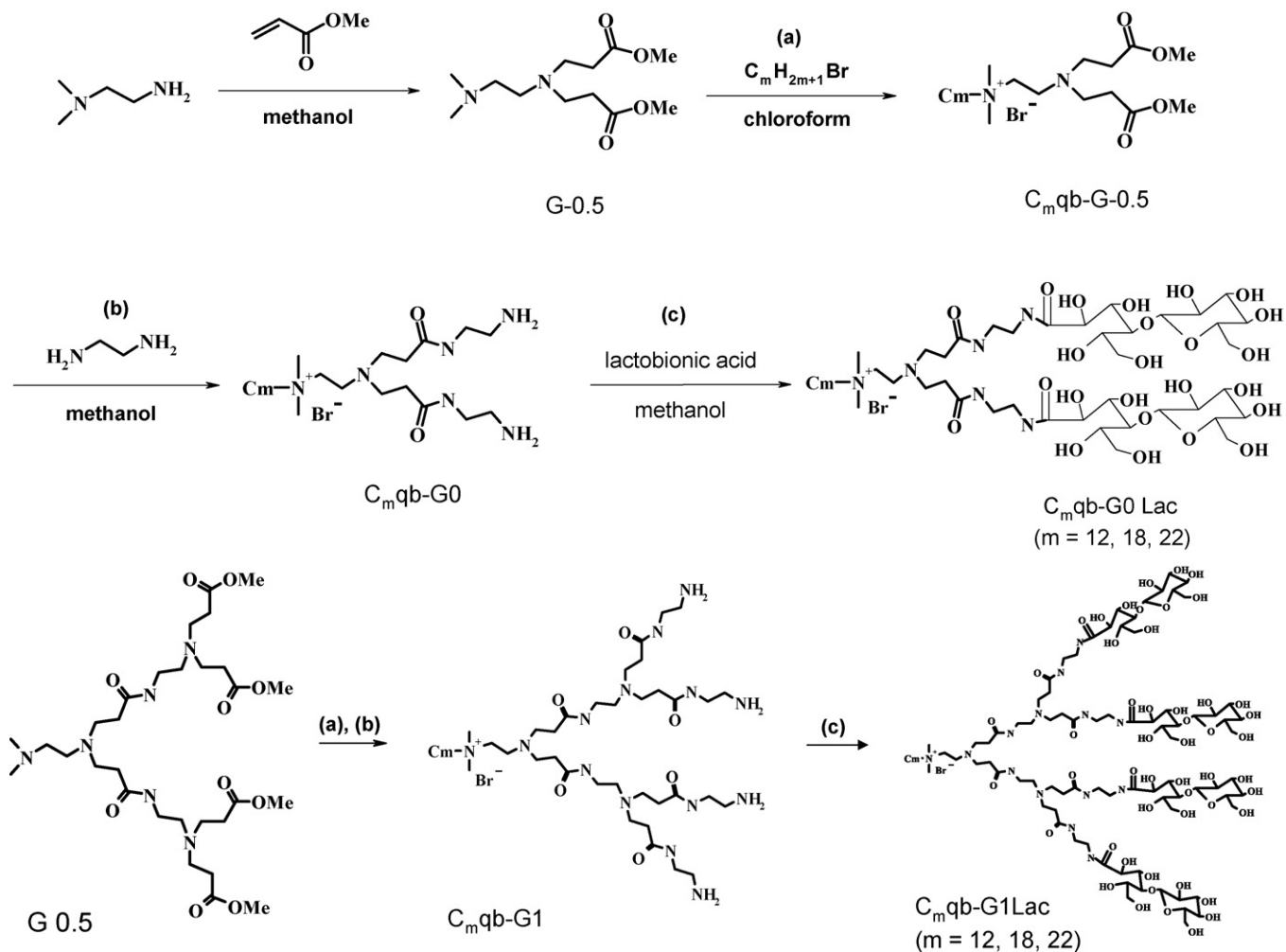
Dendrons are umbrella-shaped polymers with regular branching units [1]. Unlike conventional random-coil polymers, dendrons have a single molecular weight and take more robust conformations. The first reported poly(benzyl ether) dendron was synthesized by a convergent method [2], while afterward divergent methods have also been applied in which molecules with non-symmetrical multifunctional groups like *N,N*-dimethylethylenediamine were utilized as a core [1,3]. Functionalization of dendron molecules have extensively been studied for various applications involving liquid crystals [4–6], catalysts [7,8], sensors [9], photovoltaics [6], drug carriers [10,11] and gene vectors [12].

On the other hand, we have previously reported that introduction of multiple octyldimethylammonium groups to amino-

terminated poly(amidoamine) (PAMAM) dendrimers endows them with surface-active properties [13–15]. These dendrimer surfactants show different properties from those of conventional cationic surfactants such as alkytrimethylammonium bromide ($C_m\text{TAB}$). For instance, in the dendrimer surfactant comprised of the 1st generation PAMAM with 16 octyldimethylammonium groups ($C_8\text{qbG1}$) [15], the surface tension vs. concentration curve exhibits two break points; one at lower concentration corresponds to the critical micelle concentration (cmc) and the other at higher concentration is supposed to be due to the adsorption of dendrimer monomers from bulk phase to a monomer layer preformed at the air/water interface. On the other hand, the dendrimer surfactant of a higher generation ($C_8\text{qbG4}$) is less surface active than that of lower generations ($C_8\text{qbG0}$ and $C_8\text{qbG1}$), due to an increasing volume of hydrophilic head groups [13–15]. These results clearly indicate that solution properties of the surfactant are strongly dependent on their molecular structure. Accordingly, comparison of the solution properties for the surfactants with different structures, i.e., dendrimer, dendron and other hyper-branched polymer structures, is very important for further understating of structure–performance relationship.

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Scheme 1.

Another interest in the present work consists of the introduction of sugar groups as head groups of surfactant [16–20]. Since sugar groups are biocompatible, sugar-based surfactants are environmentally benign, thus they can find various applications including cosmetics, detergents, and biomedical materials. We have synthesized some single chain, gemini and dendrimer surfactants with sugar headgroups and studied their physicochemical properties [21–25].

Herein we synthesized PAMAM dendron surfactants bearing a focal quaternary alkyldimethylammonium group and terminal sugar groups (refer to as $C_m qb-G_n Lac$) with alkyl chain length $m = 12, 18, 22$ and generation of the dendron $n = 0$ and 1. Solution properties have been investigated by means of surface tension, fluorescence probing with pyrene, electric conductivity, dynamic light scattering (DLS) and static light scattering (SLS).

2. Experimental

2.1. Materials

N,N-Dimethylethylenediamine, methyl acrylate, ethylenediamine, 1-bromododecane, 1-bromooctadecane, 1-bromodocosane and pyrene were purchased from TCI. DL-Lactobionic acid was provided from Aldrich. Methanol, chloroform, hexane and dimethylsulfoxide were purchased from Wako Pure Chemicals. Diethylether was purchased from Showa Kogyo. All chemicals

were of reagent grade and used without further purification. Water was deionized with a Barnstead NANO pure Diamond UV system (resistivity > 18.2 M Ω cm).

2.2. Synthesis of $C_m qb-G_n Lac$

The PAMAM dendron surfactants were synthesized as shown in Scheme 1, referred to Tomalia's divergent method [1,26]. For the first step, Michael addition was applied for *N,N*-dimethylethylenediamine (40.0 g, 0.454 mol) by dropwise addition of methyl acrylate (80.6 g, 1.13 mol) in methanol at 0 °C under nitrogen, then the reaction was conducted at 40 °C for 24 h. Then the reaction mixture was distilled under reduced pressure to remove methyl acrylate in excess, whereby PAMAM dendron G-0.5 bearing 2 methyl ester terminals was yielded.

For the second step, a large excess of ethylenediamine (172.0 g, 1.95 mol) was added dropwise to PAMAM dendron G-0.5 (20.0 g, 7.80×10^{-2} mol) in methanol at 0 °C under nitrogen, and the reaction was conducted at 40 °C for 96 h. Then the reaction mixture was distilled under reduced pressure to remove ethylenediamine in excess, whereby PAMAM dendron G0 bearing 2 amino terminals was obtained. Successively the first procedure was repeated to yield PAMAM dendron G-0.5 with 4 methyl ester terminals.

For the third step, an alkyl chain was introduced to the focal point of the dendrons by dropwise addition of 2.5 mol equiv. of 1-bromoalkane ($m = 12, 18, 22$) to PAMAM dendron G-0.5 (20.0 g,

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