Synthesis of polysaccharide derivatives forming narrow size-distribution flower micelles and structural analysis in aqueous solution

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Abstract

Succinic acid derivatives of polysaccharides, including modified starches, are widely used as emulsifying stabilizers. Although these derivatives have been suggested to form micelle structures in aqueous solutions, their micelle structures are presumed to be non-uniform, and detailed structural determination remains rare. To address this issue, this study successfully prepared uniform micelle structures by reacting pullulan, a type of polysaccharide, with succinic anhydride containing saturated alkyl groups. As shown in Figure 2, the formation of flower micelle structures was confirmed. Furthermore, varying the pH of the aqueous solution from 7 to 10 led to partial ionization of hydroxyl groups in the sugars, resulting in a smaller micelles formation.

Background & Results

The formation behavior of molecular aggregates, such as polymeric micelles, is strongly influenced by weak intra- and intermolecular interactions that depend on temperature and solvent composition in aqueous solutions. Solution scattering experiments using quantum beams (e.g., light, X-rays, and neutrons) are effective for observing these behaviors. However, data from such measurements often reflect the average characteristics of numerous molecular aggregates in solution, making accurate structural determination challenging when size and shape distributions are wide.

Previous studies demonstrated that synthetic amphiphilic polymers with randomly arranged hydrophobic groups can form relatively uniform micelle structures, and their precise structural details have been determined. However, micelle structures formed by succinic acid derivatives of polysaccharides synthesized using conventional methods often exhibit broad structural distributions due to the heterogeneous nature of the aqueous reaction system, making precise structural determination difficult. Additionally, with increasing environmental concerns over the poor biodegradability of synthetic polymers, the detailed structural analysis of natural polymer-derived amphiphilic polysaccharides is of growing importance for elucidating the relationship between their structure and physicochemical properties.

In this study, succinic acid derivatives of pullulan were successfully synthesized using solvent systems previously applied for polysaccharide carbamate derivatives. Small-angle X-ray scattering measurements revealed characteristic scattering data consistent with polymeric micelles (Figure 3). Data analysis demonstrated that the “flower necklace micelle” model (Figure 2) accurately reproduces the experimental results. The formation of these structures was attributed to the consistent number of sugar units per flower micelle regardless of polymer chain length. Additionally, pH-induced structural changes were successfully observed, facilitated by the uniformity of the micelles, overcoming challenges associated with conventional methods.

Future research will focus on studying micelle structures formed by different backbone structures, substituent groups, and substitution degrees in polysaccharides to reveal correlations between chemical structures, micelle morphologies, and functional properties, such as emulsification capabilities. Furthermore, these findings may be applied to determine micelle structures in samples synthesized using conventional methods.

Significance of the research and Future perspective

Polysaccharides modified to possess amphiphilic properties are not only used as emulsifying stabilizers but are also extensively studied as drug delivery materials. However, polysaccharides industrially produced for food applications often exhibit non-uniform micelle structures, which limits their suitability for precise structural analysis. This study improved conventional synthesis methods and successfully formed uniform micelle structures. Detailed analysis elucidated the mechanisms behind micelle formation caused by the introduction of substituent groups. These findings suggest that the developed micelle structures have significant potential applications as emulsifiers in food, cosmetics, and pharmaceutical industries.

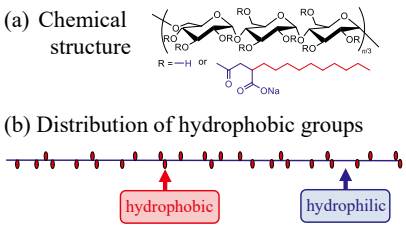

Figure1. (a) Chemical structure of decyl succinic anhydride-modified pullulan (PulDS). (b) Schematic representation of distribution of hydrophobic groups.

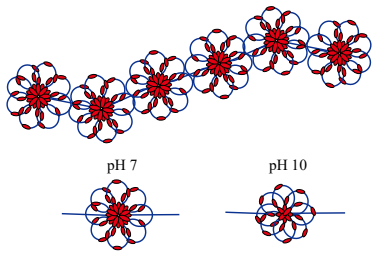

Figure 2. Schematic diagram of the flower necklace-type micelle structure in aqueous solution and its pH change.

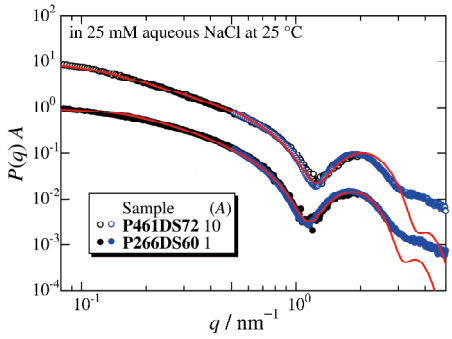

Figure 3. $P(q)$ data for the indicated PulDS samples and theoretical values of flower necklace model for polymer micelles in 25 mM aqueous NaCl.

Patent

Treatise Suenaga, Risa; Komuro, Yuzu; Terao, Ken. Highly soluble and well-defined polysaccharide-based micelle in aqueous media: Decyl succinic anhydride-modified pullulan. Carbohydr. Polym. 2025, 358, 123504. doi: 10.1016/j.carbpol.2025.123504
Sato, Takahiro; Yang, Jia; Terao, Ken. Micellar structure of hydrophobically modified polysaccharides in aqueous solution. Polym. J. 2022, 54, 403-412. doi: 10.1038/s41428-021-00561-4

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Keyword polysaccharides, amphiphilic polymers, micelles, food additives