Medical & healthcare, Separation/purification

Molecular recognition of polysaccharide derivatives with highly branched architecture

Department of Macromolecular Science, Graduate School of Science

Professor Ken Terao

Researchmap https://researchmap.jp/kenterao?lang=en

Abstract

Highly branched polysaccharide derivatives consisting of rigid rod-like chains were synthesized. Their dimensional and hydrodynamic properties in organic solvents were investigated by light and X-ray scattering and viscometry. The obtained radius of gyration and intrinsic viscosity were found to be much smaller than those of linear chain with the same molar mass. The chiral columns with this hyperbranched sample coated on silica particles showed chiral recognition ability for a number of racemic compounds, confirming its high chiral separation ability. It was also clarified that the chiral separation ability is appreciably different from those of linear chains, indicating the difference in molecular recognition ability. This is because the hyperbranched structure, consisting of rigid and densely branched chains, distorts the rigid helical structure.

Background & Results

Polysaccharide derivatives are used in a wide range of applications from foods and commodities to fibers and resins. Among them, carbamate derivatives of polysaccharides are widely used as chiral stationary phase for chiral separation columns, which are decisively important for purification and purity determination of low-molecular-weight chiral compounds used in pharmaceuticals. Since the chiral separation ability of polysaccharide derivatives is related to the helical structure of the polysaccharide main chain, it was expected that the separation ability would also be affected when differences in the architecture of the polymer chain affect the helical structure. Therefore, in this study, polysaccharide carbamate derivative samples with a hyperbranched structure were synthesized using commercially available highly branched cyclic dextrin samples. The above-mentioned difference in chiral separation ability was observed in the investigated carbamate derivatives.

Branched and cyclic polymers consisting of rigid chains have not yet been studied extensively. Considering the recent development of novel polymer synthesis, it is expected that such polymers will become readily synthesizable to develop novel functions.

Significance of the research and Future perspective

The molecular size and viscosity in solution of the hyperbranched polymers are much smaller than those of the linear chain with the same molar mass. This viscosity ratio becomes more pronounced for rigid chains. In the case of the present study, the intrinsic viscosity was about 1/40 times that of the linear chains. This low viscosity allows us to readily handle high molecular weight polymer solutions. The distortion of the helical structure of the rigid hyperbranched chains has a pronounced effect on the interaction with solvent molecules as well as on the chiral separation. In fact, phase separation was also observed for hyperbranched chains even in a solvent at which the corresponding linear chain was fully dissolved. We expect to develop novel functions with the hyperbranched structure that cannot be achieved with only linear chains.

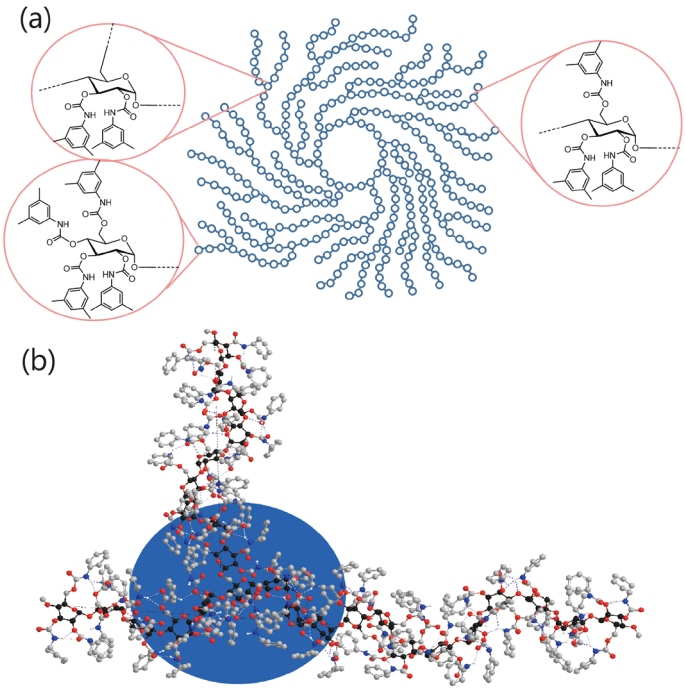

Figure 1. (a) Chemical structure of the highly branched polysaccharide derivatives and (b) schematic image of the branching point.

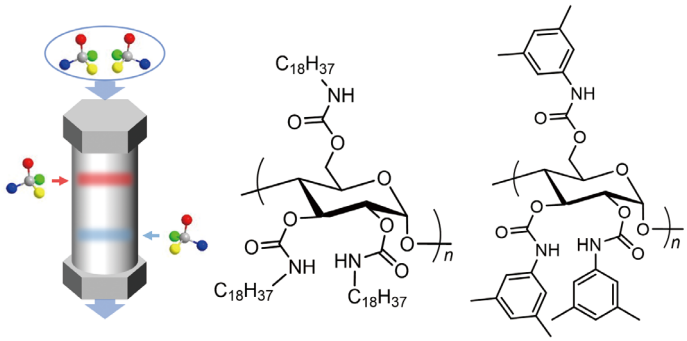

Figure 2. Schematic representation of the chiral column and the chemical structure of the polysaccharide derivatives used as chiral stationary phases.

Patent

Treatise

Kishimoto, Aika; Ryoki, Akiyuki; Terao, Ken et al. Molecular structure and chiral recognition ability of highly branched cyclic dextrin carbamate derivative. Carbohydr. Polym. 2022, 290, 119491. doi: 10.1016/j.carbpol.2022.119491

Kishimoto, Aika; Ryoki, Akiyuki; Terao, Ken et al. Correlation between conformational feature in solution and chiral separation ability of linear and nonlinear amylose tris(alkylcarbamate)s. Polymer. 2023, 284, 126303. doi: 10.1016/j.polymer.2023.126303

Mizuguchi, Madoka; Umeda, Keisuke; Terao, Ken et al. Solution characterization of a hyperbranched polysaccharide carbamate derivative and specific phase separation behavior due to chain branching. Soft Matter. 2023, 19, 7781-7786. doi: 10.1039/d3sm01074k

URL https://www.chem.sci.osaka-u.ac.jp/lab/terao/

Keyword polysaccharide derivatives, branched polymers, stiff chains, molecular recognition, chiral separation