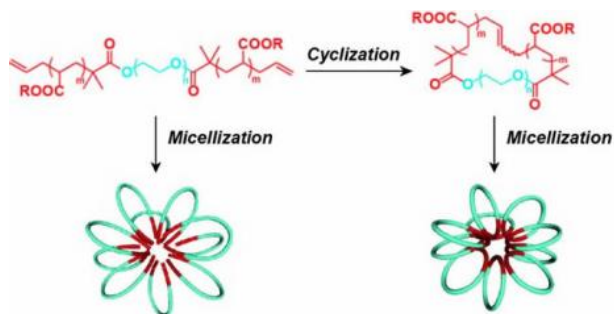


Coming round to stable self-assembly

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The team used linear and cyclic block copolymers to create flower-shaped micelles. The cyclic-based micelles withstood considerably higher temperatures and salinity levels, and could have numerous applications in industry and green chemistry.

Nanostructures that assemble themselves from polymer molecules could prove to be useful tools in chemistry and industry. However, it is difficult to develop structurally robust self-assembling materials because they are often adversely affected by their surroundings.

Many [natural organisms](#) have evolved to protect themselves in hostile environments. For example, types of archaea - single-cell microorganisms living in hot springs - have cyclic molecules in their cell membranes that form shields to preserve the cell under [extreme heat](#).

Inspired by nature's use of cyclic structures, Takuya Yamamoto and co-workers at the Department of Organic and [Polymeric Materials](#), Tokyo Institute of Technology, have dramatically enhanced both the thermal and salt stability of self-assembling polymeric structures, simply by changing the shape of the founding polymers from linear to cyclic.

The team designed new block copolymers - structures comprising several polymers connected by covalent bonding - which self-assembled into

shapes called micelles (Fig.1). Micelles have a hydrophilic (water-attracting) [outer membrane](#), and a hydrophobic (water-repelling) core.

"We designed a cyclic amphiphilic block copolymer by mimicking fat molecules in the [cell membrane](#) of archaea," explains Yamamoto. "Both linear and cyclic copolymers were then used to create identical self-assembling flower-shaped micelles." The team discovered that although the [chemical composition](#), concentration and dimensions of micelles built from the two differently shaped block copolymers remained the same, the cyclic-based micelles were able to withstand higher temperatures.

"The micelle from cyclic [block copolymers](#) withstood temperatures up to 40°C higher than the linear-based micelles," explains Yamamoto. The researchers found that the tail ends of the linear copolymers were more likely to break loose from the flower-shaped structure during heating, allowing for bridging between micelles to occur. This meant that the micelles join together in an agglomerate blob at a relatively low temperature. The micelles created by the cyclical copolymers, on the other hand, had no 'loose ends' to form bridges, meaning the structures remained stable up to far higher temperatures.

The same structural differences allow for a greater tolerance of salt concentrations in the cyclic-based micelles. The loose tails in linear-based micelles allowed rapid dehydration to occur in highly saline environments, whereas the closed cyclic structures are structurally stronger, making them more resilient to salt.

"The combination of higher salting-out concentrations and thermal resistance means these micelles have numerous potential applications," explains Yamamoto. "Possibilities include drug delivery systems, where heating is not possible and salt provides an alternative method for controlling how a micelle responds in order to release a drug." The team also hope that their micelles could

provide the basis for many new materials in the field of green chemistry, because their structural robustness is based purely on their shape rather than on complex chemical reactions.

More information: Honda, S. et al. Topology-directed control on thermal stability: micelles formed from linear and cyclized amphiphilic block copolymers. *JACS Communications*, published online July 2010.

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