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Janus regulation of ice growth by hyperbranched polyglycerols generating dynamic hydrogen bonding

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In this study, a new phenomenon describing the Janus effect on ice growth by hyperbranched polyglycerols, which can align the surrounding water molecules, has been identified. Even with an identical polyglycerol, we not only induced to inhibit ice growth and recrystallization, but also to promote the growth rate of ice that is more than twice that of pure water. By investigating the polymer architecture and population, we found that the stark difference in the generation of quasi-structured H_2O molecules at the ice/water interface played a crucial role in the outcome of these opposite effects. Inhibition activity was induced when polymers at nearly fixed loci formed steady hydrogen bonding with the ice surface. However, the formation-and-dissociation dynamics of the interfacial hydrogen bonds, originating from and maintained by migrating polymers, resulted in an enhanced quasi-liquid layer that facilitated ice growth. Such ice growth activity is a unique property unseen in natural antifreeze proteins or their mimetic materials.

Water freezing is a commonly observed natural phenomenon; however, ice growth and recrystallization can critically damage living organisms[1]. Nature has evolved to produce antifreeze proteins (AFPs)[2] to survive this freezing threat. Their specific amino acid sequence has been widely accepted to play a critical role in binding to ice[3–9], which can result in antifreeze activity when the Kelvin effect is dominant at the ice interface. To date, various studies mimicking the unique antifreeze activity of AFPs have been reported by using glycoproteins[10], carbohydrates[11,12], polymers[13–18], supramolecules[19], carbon materials[20–22], and gold nanoparticles[23]. On the contrary, ice-binding surfaces can also lead to heterogeneous ice nucleation when the appropriate chemical and dimensional aspects are satisfied. Ice nucleation proteins and their mimics possess a large ice-binding surface, which facilitates the organization of surrounding water molecules in an ice-like lattice that could promote ice nucleation[24–30]. Cryosurgery utilizing such promoted ice growth within cells has been suggested[31,32]. The effects of surface size, shape, and material type on antifreeze or ice nucleation were investigated through computational analyses[33–36]. Both phenomena, which require ice-binding characteristics in common, demand distinct design protocols, and thus active materials have been developed by tailoring them for respective purposes. In this work, we report a single type of hyperbranched polymeric agent that exhibits both promotion and inhibition activities. The polymer's formation–dissociation dynamics of hydrogen bonds (H-bonds) with the ice interface regulated ice growth in opposite tendencies depending on its population.

Results

Janus effect of polyglycerols on ice growth and recrystallization

We selected hyperbranched polyglycerol (*hb*PG) to realize the Janus effect on ice growth and recrystallization. Owing to its unique three-dimensional architecture, which comprises a polyether backbone with several functional hydroxyl groups, along with its excellent biocompatibility and immunogenicity[37], *hb*PG has gained significant

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