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POLYMER MIMICS OF BIOMACROMOLECULAR ANTI FREEZES

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ABSTRACT

Antifreeze proteins are biopolymers which are produced by some plants, insects, vertebrates, fungi & bacteria and these help surviving in sub zero temperatures. These proteins inhibit growth and recrystallization of ice crystals which are fatal for life process. Research in this field is of importance as in the fields of cryosurgery and cryopreservation of tissues , prevention of ice growth on wind turbines & on aeroplane wings and to find out better technologies for frozen foods, we need to understand how in nature the antifreeze proteins work and what are their structures and properties. This review paper discusses various progresses in this field in recent times which is aimed to encourage further research in the field of biodegradable antifreeze compounds. In these times of high environmental pollution it is highly relevant to synthesize biopolymers which will not negatively impact the environment but at the same time help solve the problem of saving the life of cells and tissues at sub zero temperatures.

Keywords: *Antifreeze Proteins, Biopolymers, Ice Structuring Proteins, Ice Restricting Proteins, Ice Recrystallisation Inhibitors*.

Introduction

Biopolymers

Biopolymers are polymers which are either found in living organisms or are synthesized by living organisms. These are biodegradable and most abundant in nature. The word biopolymers indicates that such compounds are biodegradable such as proteins, carbohydrates, polysaccharides, lipids, polypeptides, nucleic acids etc. Cellulose is the most common biopolymer in nature and it is approximately 33% of all plant component on earth.

Types of Biopolymers and their Benefits

Basically biopolymers are of two types, one which are obtained from living organisms like carbohydrates, protein, cellulose, Chitin, starch etc. and the other which are produced by polymerization of the compounds obtained from natural resources eg. petroleum based PVA, plastic acid, carbohydrates etc. Environmental benefits of biopolymers lie in the fact that they are carbon neutral and they can always be renewed, biodegradation of these biopolymers release carbon dioxide, which can be used by the plants grown and substitutes in their place.

Antifreeze Proteins or Ice Restricting Proteins

Ice is a big problem for those organisms which live in cold climates. Once the temperature dips below freezing point, ice crystals steadily grow and burst cells. Organisms of types, plants, animals, fungi and bacteria have developed ways to combat deadly growth of ice crystals. Some pack their cells with small antifreeze compounds like sugars or glycerol. But where these don't work, then cells make specialised antifreeze proteins to protect themselves from temperature drops. These antifreeze proteins (AFPs) don't stop the growth of the ice crystals, but they limit the growth to manageable sizes, that is why they are called as ice restricting proteins.

Recrystallisation

When crystals start forming, a few crystals dominate and not only grow larger and larger but also steal water molecules from surrounding small crystals and this process is called recrystallization. Antifreeze proteins counter this recrystallization effect by binding to the surface of the small ice crystals and either slow or prevent their growth in to larger fatal crystals. AFPs also interact with mammalian cell membranes to protect them from cold damages.

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Thermal Hysteresis

There is another phenomenon which is brought about by the antifreeze proteins, namely, thermal hysteresis. Antifreeze proteins lower the freezing point of water by a few degrees, but they don't change the melting point of water. This process of decreasing the freezing point but not affecting the melting point is called thermal hysteresis.

Mode of Action of AFPs and their Structure

AFPs or ice structuring proteins (ISPs) are polypeptides produced by certain vertebrates, plants, fungi and bacteria, which permit their survival in sub zero temperatures. AFPs help in cold acclamatization by binding to small ice crystals to inhibit growth and recrystallization of ice crystals in cells, which is otherwise fatal.

Antifreeze automotive compounds lower freezing points in proportion to concentrations but AFPs don't act like that. AFPs can act at concentrations of 1/300th to 1/520th of those of non biopolymeric compounds. Thermal hysteresis is a difference between melting point and freezing point, the maximum level of thermal hysteresis is shown by fish AFPs (-1.5 approximately) , whereas insect antifreeze proteins are ten to thirty times more active than fish proteins. There are plant AFPs, insect AFPs, sea organisms AFPs.

Ice growth damages cells during cryopreservation of tissues and cells and ice growth on wind turbines, on aeroplane wings and in frozen foods.

AFGPs i.e. antifreeze glycogen proteins are expensive, cytotoxic and potentially immunogenic, which makes synthetic mimics important. Short glycopeptides with simplified amino acids sequence are crystallization inhibitors (IRIs) but they don't show any ice shaping, which means that specific receptor-ligand type of interaction is not essential for IRI. This also indicates that more diverse structures could be more useful.

Surfactant polyvinyl alcohols, polyampholytes etc. have been found to show IRI properties. These IRI active compounds highly improve cryopreservation of cells and reduce the concentration of the concentration of toxic organic solvents, used in conventional cryopreservation. Many AFPs have amphilic-a- helix structures with facial amphicity. Saffron O has been found to mimic AFPs by self assembling into an amphipathic fibre. Helicals, which are multimetallic, multistrand coordination complexes resemble alpha helix in terms of diameter and charge.

Many metallohelical enantiomeric AFPs with pharmacological properties have been synthesized, with properties like nucleic acid binding, enzyme inhibition, anticancer and antimicrobial properties, which can be used in transfusion and basic biomedical researches.

Triplex metallohelical with assymetric amphipathic structure and IRI properties have been also synthesized. These are water soluble compounds which are constructed from hydrophobic ligands with IRI activities due to metal ions. Triplex metallohelices are synthetically more accessible than glycopeptides and they have more benefits over polymeric inhibitors due to the fact that they have no molecular weight desparity. Moreover different heterocyclics and arenes have been found to provide scaffold like structure.

Nature has has evolved many amazing solutions to enable life at low temperatures by preventing ice formation or by controlling ice nucleating proteins or antifreeze proteins, which either act to prevent nucleation or inhibit ice growth. These proteins may sometimes be expensive.

Polyvinyl alcohol (PVA) has been investigated for ice nucleation inhibiton(INI) activities and its activities are compared with many biopolymers. Particular stress is placed on designing polymers which have no structural similarities to antifreeze proteins but reproduce the same macroscopic properties. PVA has been most investigated polymeric IRI (ice recrystallisation inhibition), hydroxy groups are not essential components in it ,which implies that a wide chemical range should be studied. PVA can be obtained from polyvinyl acetate. PVA is a challenging polymer as it is not easy to polymerise and limited functional groups can be introduced in to it, also removal of acetate groups need harsher conditions. It has been found that polyampholytes, polymers mixed with cationic and anionic groups are remarkable cryo preservatives and influence ice crystal formation at higher concentrations. Polyaminoethyl methacrylayte and carboxylated polysaccharides are IRI active polymers. Carbon nanoflakes and carbon nanotubes are also IRI active. Similarly polyhydroxyethyl acrylamide, poly-N- isopropyl acrylamide, polyoligo ethylene glyco methacrylayte have been studied for their IRI properties.

Focus has also been on designing polymers which have no structural similarities to antifreeze proteins but reproduce the same macroscopic properties, potentially by different molecular level mechanism. The application of these polymers to the cryopreservation of donor cells is also important. Ice recrystallization inhibition is more easily done with a diverse range of polymers, supramolecular assemblies or small molecules, although no structural similarities are present between these molecules. Applications of IRI in cellular cryopreservation is particularly important, where slowing the growth of ice during thawing had been found to lead to remarkable enhancements in cell recovery post storage, which proved that these are innovative solutions to the logistical challenges associated with emerging regenerative medical treatment .These advances have triggered renewed interest in this area and it is anticipated that as more research groups enter this exciting and highly interdisciplinary field , advances will continue to the point where synthetic materials may be able to out perform the natural proteins.

This review has summarised the current state of the art in rapidly emerging field of synthetic macromolecules which can mimic the functions of antifreeze glycoprotein. Recent developments in polymer chemistry have enabled a wide range of polymers to be assessed for these properties but still a large number of such polymers are being discovered. It has become clear that the precise primary sequence and 3D structure of natural antifreeze is essential for thermal hysteresis and ice shaping, which means that molecular recognition type mechanism occurs on ice crystal surface. Ice recrystallization inhibition is more easily done with a diverse range of polymers, supramolecular assemblies or small molecules, although no structural similarities are present between these molecules. Following key challenges need to be addressed for the field to continue to advance:

Do several molecular level mechanism give rise to the macroscopic effects and if so, can these be separated? Do polymeric mimics function by the same mechanisms as AF(G)Ps? What is the role of amphipathicity in IRI? Is there a minimum or maximum IRI activities required to increase cell cryopreservation?

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