Energy-Rich Forms of Solid Cyclodextrins

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The solid-state cyclodextrins and their complexes constitute more than half of the industrial applications. The important property of cyclodextrins is their ability to solubilize poorly soluble guests, which requires the cyclodextrin forms with high solubility properties. This is a problem for natural cyclodextrins which have a relatively poor solubility and a slow rate of dissolution in water. The improved solubility properties can be achieved using the metastable polymorphs or amorphous forms. Also, a solid-state interaction with energy-rich forms of cyclodextrins can be a greener alternative to the techniques used in the present industries since such interaction requires no solvent or excessive energy. Thus, search for energy-rich forms of cyclodextrins may be of practical importance.

The solid-phase guest exchange in ternary systems produces an amorphous inclusion compound whose heating gives a true amorphous α-cyclodextrin without any traces of its crystalline phase[1]. This is the first evidence of α-cyclodextrin amorphization using supramolecular techniques. It can be used in practical applications where the amorphous state is needed to bring a higher inclusion capacity. The new method is a much greener alternative to the milling or spray drying widely used nowadays.

The new-found[2] polymorph of β-cyclodextrin was prepared through endothermic transition by heating of the dried commercial form of β-cyclodextrin. The new polymorph has a triclinic cell with an essentially different packing than that of conventional β-cyclodextrin. The new polymorph is energy-rich: its formation has a positive enthalpy and Gibbs energy change at 25 °C. The dissolution of new polymorph in liquid water is many times faster than that of the conventional form of β-cyclodextrin. Also, the new polymorph dissolves in water vapors at the same humidity as the highly water-soluble HPβCD and has a higher affinity for water than the conventional form of β-cyclodextrin. Thus, the new polymorph can be used for preparation of inclusion compounds in pastes or for a quick removal of undesirable compounds from water being a cheaper alternative to the chemically modified β-cyclodextrin.

The high activation energy of the polymorphic transition creates a possibility to stabilize the polyamorphism of β-cyclodextrin. The amorphization by ball milling of the new polymorph results in formation of a new polyamorph. This is the first evidence of polyamorphism for supramolecular hosts. Such polyamorph provides the highest possible energy state of solid β-cyclodextrin what results in, e.g., improved inclusion properties.

References

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