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Molecularly Imprinted Polymers as Selective Sorption Materials for Preparation Application: Strategy to Created Homogeneous Selective Binding Sites by Non-Covalent Imprinting

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Abstract

The problem of creating selective sorbents by non-covalent molecular imprinting is the formation of homogeneous high-affinity binding sites due to the complexity of the functional monomer - template complex formation, as well as the formation of additional complexes with the components of the prepolymerization mixture. The solution could be the creation of a structurally stable polymer matrix with the possibility of purposefully changing the functionality of binding sites for templates of various nature with the right choice of components of the prepolymerization mixture.

Keywords: Polymer Sorbents; Molecularly Imprinting; Selectivity; Binding Sites; Polymer Network; Structure Stable

Introduction

Selective sorption materials are used in various areas affecting human life, such as ecology, industry, medicine and al. [1-3]. In ecology aspects, their used is possible to purify industrial effluents to environmentally friendly ones, purify natural water resources from already accumulated pollutants, and obtain drinking water. In industry, their use makes it possible to produce high-purity individual substances, for example, drug substances of pharmacopoeial purity in a one-act mode, which reduces the use of polluting organic solvents. In addition, they used as plasma- and hemosorbents, which are used in efferent methods of blood purification from toxins of both endogenous and exogenous nature. For example, for the treatment of diseases as diabetes mellitus, sepsis, gout, hypercholesterolemia, etc. or intoxications of the organism. Their mechanism of action is based on the selective binding of target molecules from a multicomponent aqueous medium. Therefore, the fundamental factor of sorption materials performance is their selectivity, which is determined by the affinity of the sorption surface of the adsorbent to the solute.

Molecular imprinting has become a method for creating highly selective binding sites that mimic natural receptors [4-10]. It consists in carrying out polymerization in the presence of target molecules (template). As a result, the polymer chains formed during polymerization self-organize around the template and, after cross-linking, are fixed in the polymer network, which leads to the appearance of imprinted cells (pores, binding sites, imprint-sites). After the removal of the template, imprinted cells remain complementary to its molecules in size, shape, and arrangement of functional groups according to the principle of a biological receptor. At the same time, unlike natural receptors, molecularly imprinted polymers (MIPs) have structural stability in a wide range of pH, ionic strength, temperature, and content of organic solvents.

Non-covalent molecular imprinting has become the most widespread in practice due to the relative simplicity of the process itself, based on non-covalent intermolecular interactions, such as hydrogen bonds, van der Waals forces, ionic or hydrophobic interactions, and others, during synthesis and subsequent incorporation. The strategy of such imprinting is the self-assembly approach, in which synthetic chemistry is practically not required, the components of the polymerization mixture (functional

monomers, cross-linking agent, target object) are simply mixed to carry out self-organization of molecules with subsequent cross-linking [11,12]. By retaining the "molecular memory" embedded in the cross-linked polymer network, imprinted cells are capable of re-embedding the target molecule. However, this approach has its disadvantages.

Conclusion

One of the main ones is the formation of heterogeneous binding sites due to the self-organization around the template molecules of not only monomers, but also oligomers, macromonomers, as well as the presence of various functional monomer and template adducts in the prepolymerization mixture [11]. As a result, along with fully complementary imprint-sites, "worse" sorption sites (partially complementary cells) with varying degrees of affinity are formed [13]. Such an affinity range is a general disadvantage that makes it difficult to work with preparative sorption materials. Therefore, in order to create highly selective preparative sorption materials, it is important to achieve binding sites that are completely complementary to the target molecule and form a homogeneous sorption surface. We achieved this by introducing template molecules of various nature (glucose, cholesterol) into the surface layer of polymer granules by varying their concentrations [14, 15].

In addition, the use of a large amount of a functional monomer leads to the formation of non-specific binding sites and, as a result, to a decrease in selectivity. This problem of nonspecific affinity can be solved by creating a universal polymer network with little or no affinity for the target molecule [16]. Moreover, this network may be capable of weak intermolecular interactions, which will play a role in the "hold and release" analytical approach and will not matter in the "hold and hold" preparative approach. Such interactions include van der Waals forces, dipole-dipole interactions, and single hydrogen bonds. However, the formation of fully complementary imprint-sites in the network leads to a significant increase in the affinity of the sorption surface [14,15]. Subsequently, selective binding sites can be formed in the universal polymer network by equimolar replacement of the main chain monomer with a monomer carrying functionality to some groups of the target molecule [16,17]. In this case, the choice of a functional monomer is of great importance, the strength and affinity of which will affect the selectivity and affinity of the polymer [12]. Therefore, the functionality of selective binding sites will be determined both by the polarity of the phases and by ion exchange.

In addition, the conformation of the template molecule depends on the conditions in which it is located; therefore, when imprinting is carried out under conditions optimal for polymerization, the imprint-sites will be complementary to the conformation of the molecule in which it was at the time of site formation. In the case of structurally stable and rigidly cross-linked networks, the transfer of polymers from one medium to another will not affect the complementarity of binding sites and the mass transfer of solute [13,14,18]. You should also take into account the effect of the synthesis method and the necessary components for its implementation on the formation of imprint-sites, namely, the complexation of the prepolymerization mixture components with the template. So, to create granules capable of improved mass transfer, suspension, emulsion polymerization is used, which involves the use of emulsifiers of various nature (traditional - starch, surfactants, and the rapidly developing use of nanoparticles). With the right choice of components, it is possible to achieve the formation of fully complementary imprint-sites for molecules of various nature using various methods of synthesis. The use of these polymeric sorbents leads to the selective extraction of target components and the implementation of regular regimes of sorption dynamics (the time of breakthrough of the target component at the column outlet increases), which is of paramount importance when scaling laboratory processes to preparative ones [13,16-19]. Thus, we create the sorption materials with structurally stable polymer network with the ability to control the functionality of selective binding sites for template molecules of various nature using non-covalent imprinting for further preparative applications.

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