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Smart membrane: preparation of molecular cavity and preferential sorption of small molecule

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Abstract

Preparation of smart membrane was carried out for an establishment of high performance separation membrane. The smart membrane contains subnano scaled molecular cavity which is constructed by polymer architecture, which is similar to the structure of small molecules separated and is aligned regularly in crystalline polymers. First the δ form complex of syndiotactic polystyrene is obtained from a solution containing good solvent, and then good solvent as guest molecule was extracted stepwisely from the δ form complex using first extraction solvent of acetone and second extraction solvent of methanol. We could prepare molecular cavities with different sizes and shapes. Sorption of small molecules into the molecular cavity demonstrated preferential sorption in a manner of Langmuir type depending on the size and shape of both small molecules and molecular cavities.

Keywords: Syndiotactic polystyrene; Smart membrane; Molecular cavity; δ form complex; Mesophase; Vapor sorption; Preferential sorption; Langmuir sorption

1. Introduction

Many types of polymeric membranes have been extensively studied [1–4]. Membranologist has interested in the process of saving energy such as separation of small molecules using polymeric membranes. The development of much higher efficient separation polymeric membranes was expected in the case of solving an environmental problem such as saving energy and removal of toxic substances. Membrane separation has been mainly treated in the field of chemical engineering and the membrane itself has been recognized as a black box so far. There have been a few fundamental studies on the relationship between performance and structure of membranes from the standpoint of polymer science and engineering. The principle of membrane separation is basically dependent on the difference of diffusion coefficient based on free volume of polymeric membranes and solubility coefficient based on the interaction of polymer–small molecules. Namely the separation performance is dependent on the difference of permeability coefficient represented by the product of the diffusion coefficient and solubility coefficient described above [1–4]. Various types of polymeric membranes are applied to various fields due to an environmental problem, although these are not complete separation membranes. These are almost amorphous rubbery or glassy polymers which have a broad distribution of free volume or micro void as shown in Fig. 1(a). A present amorphous commodity polymeric membrane shows ineffective separation ability which is determined by the difference of diffusion or permeation based on the broad distribution of free volume or micro void. Separation performance is basically controlled by the broad distribution of free volume or micro void. On the other hand, an enzyme contains well defined molecular cavity which fits specifically to a substrate to appear specificity. At the present time there are no enzyme type synthetic polymeric membranes. Development of further high performance polymeric membranes are expected in academic and industrial laboratories in order to improve environment and saving resources and energies.

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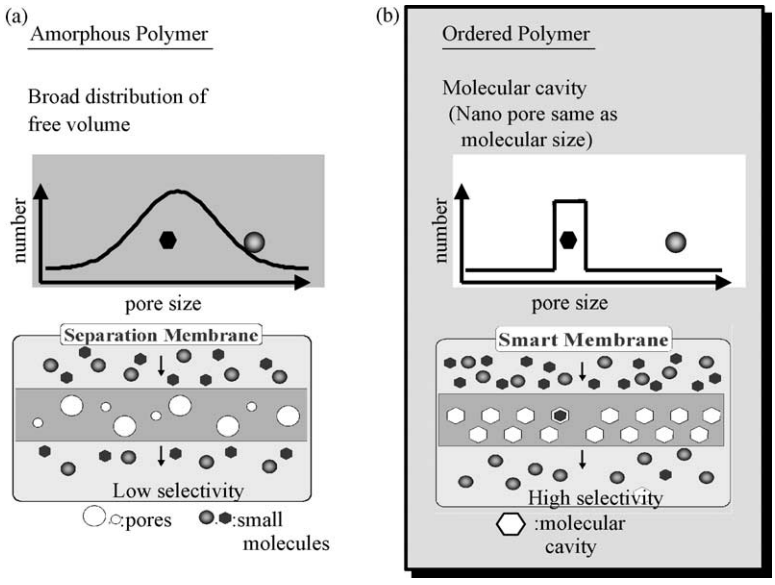

Fig. 1. Schematic representation of (a) commodity polymeric separation membrane and (b) novel smart membrane.

If one restricted membrane materials to amorphous polymer, one cannot develop polymeric membrane with much narrower distribution of free volume or micro void. One might have to change the kind of polymers. One choice is focussing crystalline polymers, especially crystalline complex polymers. We are interested in the much narrower distribution of free volume or micro void which are regularly ordered in crystalline polymers and investigate gas sorption, diffusion, and permeation through crystalline polymer of poly 4-methyl-1-pentene. Furthermore, we can design the smart membrane with much narrower distribution of void and well aligned void as shown in Fig. 1(b). Once we could prepare such a smart membrane, we might be able to obtain high performance separation ability. Molecular cavity is here defined by the nano sized micro void as a restricted molecular space which is retained as the space similar to the shape and size of single small molecule in polymeric membranes or as a structurally fitted molecular space in a manner of lock and key of an enzyme by the interaction between polymer and substrate substances. Preparation of the molecular cavity of which the size and shape is controlled definitely and a clarification of mechanism of permselectivity are very important from the physical chemical standpoint of the interaction between polymer and small molecule and transport properties of diffusion and permeation through polymeric membrane. These are associated with not only membrane performance, but also physical chemistry of smart membrane. In this article, we introduce our recent studies on the preparation method of smart membrane with novel type of cavity and preferential sorption behavior of organic solvent vapor into molecular cavity in a smart membrane. Molecular inprinted membrane, syndiotactic poly(methyl methacrylate) and polystyrene are considered as a candidate. Cavity in a molecular printed membrane is oriented at random and does not give rise to function such as high separation. Although syndiotactic poly(methyl methacrylate) might provide a potential formability of molecular cavity, it has not been studied systematically and comprehensively. In the article we do not treat syndiotactic poly(methyl methacrylate) but introduce the comprehensive studies on syndiotactic polystyrene.

2. Crystalline modification of syndiotactic polystyrene

Ishihara [5,6] et al. developed a catalyst for polymerization of syndiotactic polystyrene (sPS) about 20 years ago and many studies on structure and physical properties of sPS were actively performed. Later sPS was commercialized. Compared with completely amorphous atactic polystyrene, sPS is an engineering plastic with the advantage of heat and solvent resistant properties. Recent sPS has approximately 99.8% syndiotacticity and crystalline nature with four types crystalline modification such as α, β, δ, and γ forms [7–29]. α and β forms take *trans–trans* (TT) conformation and on the other hand δ and γ forms form *trans–trans–gauche–gauche* (TTGG) helical conformation in crystalline state. α and β forms are crystallized from either molten state or dilute solution of a certain solvent. β form constructs rhombohedral crystalline unit lattice composed of packed chain of TT conformation (density 1.068 g/cm^3) [30–49]. There is no space similar to small molecule in crystalline unit lattice of β form. One cannot prepare molecular cavity from β form. On the other hand, α form forms coarse hexagonal crystalline unit lattice of TT chain conformation (density 1.033 g/cm^3). Fig. 2 demonstrates crystalline structure of two types of α form (α' form and α'' form). One can observe a regularly consecutive channel like molecular cavity between polymer chains along with a polymer chain axis [30,50,51]. δ form is usually prepared