Molecular and Supramolecular Dynamics - a Versatile Tool for Self-Organization of Polymeric Membranes Systems

*Adinela Cazacu, Andreea Pasc-Banu, Mihail Barboiu**

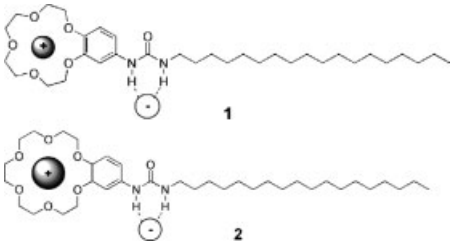
Summary: The present results show that the self-organization properties in the membrane phase may provide the first evidence for the possible hybrid transport carrier *vs.* channel mechanisms in correlation with self-assembly properties of the heteroditopic receptors. These dynamic self-organized systems can be tested in liquid membranes, bilayer membranes, mesoporous structures materials or "frozen" in a polymeric hybrid matrix by sol-gel process, opening the door to the design of a novel class of organic-inorganic nanomembranes.

Keywords: membrane; mesopores; self-assembly; supramolecular polymers

Introduction

The chemistry of membrane transport systems of interest for molecular information transfer has been extensively developed during the last twenty years. The membrane selectivity may be induced either by carrier molecules or by transmembrane channels.

From the mechanistic point of view, we use carriers which self-assemble into functional aggregates which could present combined (hybrid) intermediate features between the former carrier-monomers and the resulted pseudo-channel-forming superstructures.



Our interest focus on hybrid solid membranes in which the molecular recognition-driven transport function could be ensured by a dynamic incorporation of specific organic receptors, non-covalently linked in a hydrophobic dense siloxane inorganic matrix. Of particular interest is the potential ability of such solid membranes to combine functional properties such as solute molecular recognition and generation by self-assembling of the directional conduction pathways at the supramolecular level.

Results and Discussions

New self-organized hybrid membranes have been prepared (Figure 1) by embedding self-organized ureidocrown-ethers 15-crown-5, 1 or 18-crown-6, 2 into silica mesoporous materials, regularly oriented along the pores of the Anodisc 47 (0.02 μm) alumina membranes as support.

In a first step, the selective recognition functions of alkali metal ions (Figure 2, left) and self organization inside regular nanochannels of about 40 Å (Figure 2 right) have been emphasized by using NMR, FTIR and X-ray diffraction techniques. The MCM41-type mesostructured powders were used as hydrophobic host matrix for physically or chemically entrapped 15-crown-5 and 18-crown-6 self-organized receptors.

In this way, based on hydrophobic and specific hydrogen bonds such as urea-urea

Institut Européen des Membranes, Place Eugene Bataillon CC047, 34095 Montpellier, Cedex 5, France
E-mail: mihai.barboiu@iemm.univ-montp2.fr

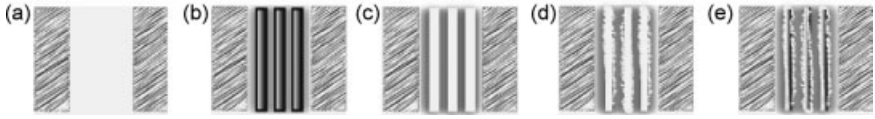


Figure 1.
Schematic representation of the synthetic route to obtain functionnalised mesostructured silica-receptor nanocomposite in the AAMs: (a) anodic alumina membrane (pore diameter ~200 nm, thickness ~60 nm, diameter of membrane = 47 mm), mesostructured silica-surfactant before (b) and after (c) calcination, ODS-hydrophobized silica before (d) and after (e) inclusion of the hydrophobic carriers **1** or **2**.

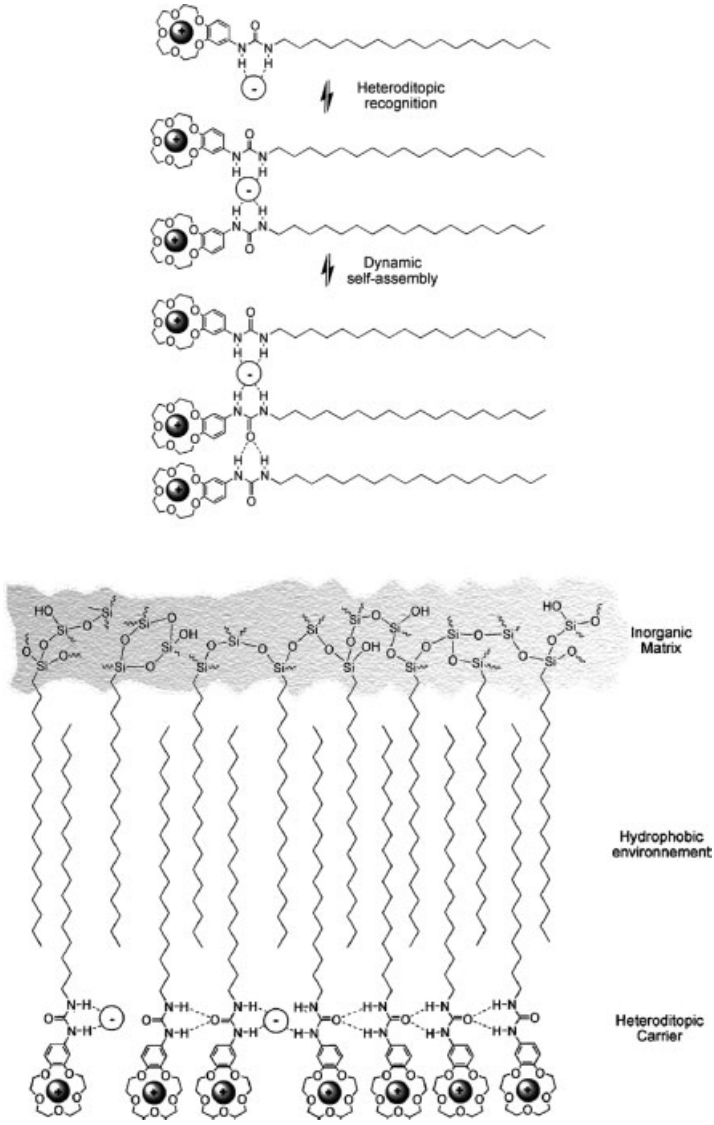


Figure 2.
Schematic representation of the hierarchical organized system **1**: (above) self-organization in solution and (below) dynamic transcription of encoded molecular features into a hydrophobic heteropolysiloxane matrix.

Table 1.
Characteristics of Na^+/K^+ transport across mesoporous functionalized membranes. **A**: CTAB/TEOS sol-gel filling of AAM (except of **M4** where **1** was introduced in the sol-gel solution precursor), **B**: thermal removal of the surfactant, **C**: octadecyltrichlorosilane (ODS) fonctionalization of silica nanotubes, **D**: functionalization with ureidocrown-ether derivatives **1** or **2**, respectively.

AAM	Permeability ($cm^2/s \times 10^8$)				Diffusion coefficient ($cm^2/s \times 10^7$)					
	Na^+		K^+		Na^+			K^+		
	P_1	P_2	P_1	P_2	$D1$	$D2$	$D3$	$D1$	$D2$	$D3$
S	8.1	0.7	25	0.8	300	20	46	552	24	48
M1	34	0.5	29	0.4	340	6	26	174	8	25
M2	40	1.5	45	1.1	3	0.003	0.09	383	25	22
M3	45	1.3	15	1.7	350	20	35	101	5	3
M4	8.8	0.2	26	0.3	310	11	18	367	16	21

or urea-anion interactions, molecular carriers can be non-covalently trapped in an inorganic matrix, which allow us to prepare very promising dynamic molecular channels.

Subsequently, organic-inorganic membranes have been prepared by filling a porous alumina membrane coupled with the sol-gel process. The MCM41-type functionalized materials were successfully oriented along the alumina membrane pores and characterized by SEM microscopy. These membranes have been tested in selective Na^+/K^+ transport.

Periodic mesoporous materials have attracted considerable attention during the last decade because of their promising applications as catalyst or as hosts for nanostructured materials. Many of these applications benefit from arrangements of preferentially aligned, ordered arrays of certain mesostructures. The evaporation-induced self-assembly method has been established as an efficient process for the preparation of thin films with mono-oriented materials.

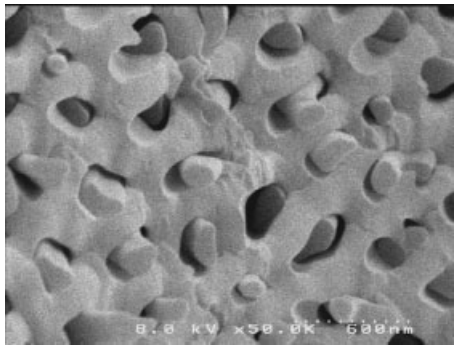


Figure 3.
Side-view SEM of alumina membrane sample M4.

However, the most frequently obtained films display hexagonally ordered channels that are aligned in a nonfavorable parallel orientation to the surface of the substrate.

Recently, the synthesis of mesoporous materials within the regular 200 nm channels of Anodisc alumina membranes (AAMs) has been explored, with the aim of attaining greater control over the morphology (orientation) of the mesoporous system. It was then demonstrated that porous anodic alumina can serve as support material to form silica-surfactant nanocomposite with a desirable orientation of nanochannels, perpendicular to the surface of the support and, consequently parallel to (along) the alumina pores.[5]

Therefore, this method was also applied by us for the preparation of our membranes, in order to allow preferentially transport nano-paths for molecules. In the first step, the AAMs were filled in with surfactant (CTAB)-template silica and then calcinated to remove of CTAB. Afterwards silica was react with ODS followed by the incorporation of long chain hydrophobic carriers.

In the absence of the silica-surfactant-receptor nanocomposite in the alumina membrane, Na^+ and K^+ cations are transported through the membrane in a similar proportion. In contrast, the hybrid crown-alumina membranes, including the silica-surfactant composite, shows a selective transport of salts depending on the receptor selectivity **1** or **2**, respectively.

The Fick law diffusion model[1] allows us to determine the transport parameters such as diffusion coefficients and permeability

across the membrane (Table 1). Moreover, in every case, we can distinguish two stages for the transport mechanism: *1*) a simple and *2*) a facilitate diffusion. In the first one, the membrane are functioning like a ''*sponge*'', and the simple rapid diffusion through the membrane is accompanied with the selective complexation of the fittest cation (Na^+ for **1** and K^+ for **2**, respectively); it is the so-called ''membrane self-preparing step''. The selective transport of the specific cation (Na^+ for **1, M2** and K^+ for **2, M3**, respectively) occurs in the second stage, much faster. Thus, one can conclude that the membrane with **15C5** receptor facilitate in the second step the transport of Na^+, whereas **18C6** receptor facilitate the transport of K^+. These experimental results suggest that the self-assembly of receptors inside the surfactant -templated silica nanochannels of the columnar alumina pores can reorganise during the molecular transport, the mechanism being characterized by an initial self-preparing step.

Conclusion

The combined features of structural adaptation in a specific hybrid nanospace and of dynamic supramolecular selection process make the membranes presented here of general interest for the development of a specific approach toward nanomembranes of increasing structural selectivity. From the conceptual point of view these membranes express a synergistic adaptative behavior: the addition of the fittest alkali ion drives a constitutional evolution of the membrane toward the selection and amplification of a specific transport crown-ether superstructure in the presence of the solute that promoted its generation in a first time. It embodies a constitutional self-reorganization (self-adaptation) of the membrane configuration producing an adaptative response in the presence of its solute. This is the first example of dynamic ''smart'' membranes where a solute induces the upregulation of (prepare itself) its own selective membrane.

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