Smart Nanocomposite Polymer Membranes with On/Off Switching Control

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ABSTRACT: Novel composite-gel membranes capable of regulating permeability in response to external temperature change are being explored. These membranes containing ordered nanochannels can act as "on−off" switches or "permeability valves". The channels are designed to contain an ordered array of core−shell type magnetic polystyrene latex particles that can change their size in response to external stimuli. Expansion and contraction of the thin shell of magnetic latex particles affect the permeation pattern from the membrane "on" state to "off" state.

Introduction

Membranes are useful tools for molecular separations because they provide a low-cost, energy-efficient green technology. Nanoscale manipulation of the membrane structure represents an innovative means to tune the membrane permeability. Hydrogels with abrupt volume change have been developed to respond to a wide variety of stimuli[1,2] and can be used to prepare valves capable of control of flow in microfluidic channels[3] "on/off" regulation of drug permeation and release.[4] The poly(*N*-isopropyacrylamide) gel, abbreviated as PNIPA gel, demonstrates a lower critical temperature (LCST) at 34 °C in aqueous solution. Below this temperature the gels swell with decreasing temperature. At higher temperature than LCST the gels shrink, demonstrating a sharp collapse transition.[5]

To prepare smart hydrogel membranes, first magnetic polystyrene latex (MPS) with 82 nm average diameter was prepared using the seed polymerization process. Then shell polymerization process was carried out to cover the surface of MPS by PNIPA. A uniform magnetic field was used to form arrays of MPS−PNIPA beads, and the channel array structures were locked by polymerization reaction in PVA gel.

Preparation of Core−Shell Type Magnetic Polystyrene Latex. Ferrofluid of magnetite (Fe_3O_4) particles with an average diameter of 10 nm was provided by University "Politehnica" of Timisoara. The magnetite concentration and the nominal magnetization of ferrofluid were 57 wt % and 596 G, respectively. The ferrofluid was mixed and stabilized with a mixture of styrene (Aldrich), sodium lauryl sulfate (Reanal), stearyl alcohol (Merck), and *N*,*N*′-azobis(isobutyronitrile) (Fluka). Magnetic polymer latex was prepared by the miniemulsion technique, and the polymerization took 12 h at 65 °C under mechanical stirring at 500 rpm. The latexes were subsequently subjected to water-vapor distillation and several rounds of washing in order to remove the unreacted monomers. Then *N*-isopropylacrylamide (NIPA) monomer, methylene bis(acrylamide) (MBA) as the cross-linker, and potassium persulfate (KPS) as the initiator were mixed with the magnetic polystyrene latex. The shell polymerization process took $^1/_2$ h at 65 °C under a nitrogen atmosphere. Thus, core−shell MPS−PNIPA microgel latex particles have been obtained with a thermosensitive PNIPA surface layer. The TEM picture in Figure 1 shows the core−shell structure of MPS−PNIPA latex in dry state. The PS core contains the magnetic nanoparticles, and the shell is made of PNIPA gel. According to the TEM pictures, the average thickness of the dry PNIPA layer was found to be 8.8 nm.

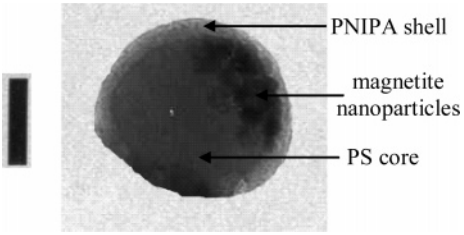

Figure 1. TEM photo of MPS−PNIPA core−shell latex in dry state. The bar indicates 66 nm.

Experimental Part

Membrane Fabrication. The MPS−PNIPA microgel latex was mixed with a 8 wt % solution of poly(vinyl alcohol) ($M_w \sim 72\,000$, Merck) (PVA) containing glutaric aldehyde (GDA) (Merck) as cross-linking agent. The cross-linking reaction of PVA was induced by lowering the pH of the solution to 2 by adding a few drops of hydrochloric acid (HCl) solution. Then the mixture was poured into a square mold with a thickness of 1.5 mm and height and width of 4 cm. The layer was placed perpendicularly to the direction of the static uniform magnetic field of $B = 400$ mT for 5 h. Because of the mutual interaction between the magnetic gel beads, a pearl chain structure develops as shown schematically in Figure 2. The cross-linking reaction locks the chainlike structure in the gel, aligned along the direction of the field. The chains of core−shell MPS−PNIPA particles form channels in the PVA matrix. In the swollen state the size of the MPS−PNIPA latex is much larger than in collapsed state. The PNIPA microgel particles undergo a collapse transition at 34 °C.[4] As a result, the swelling degree decreases drastically above 34 °C.

Results and Discussion

The PVA hydrogel is an ideal matrix of the composite membranes because in the studied temperature range no significant swelling or shrinking occurred. Increasing the temperature several times above and below the transition temperature, we never observed MPS−PNIPA beads releasing the membrane. This means that the entanglements between PVA

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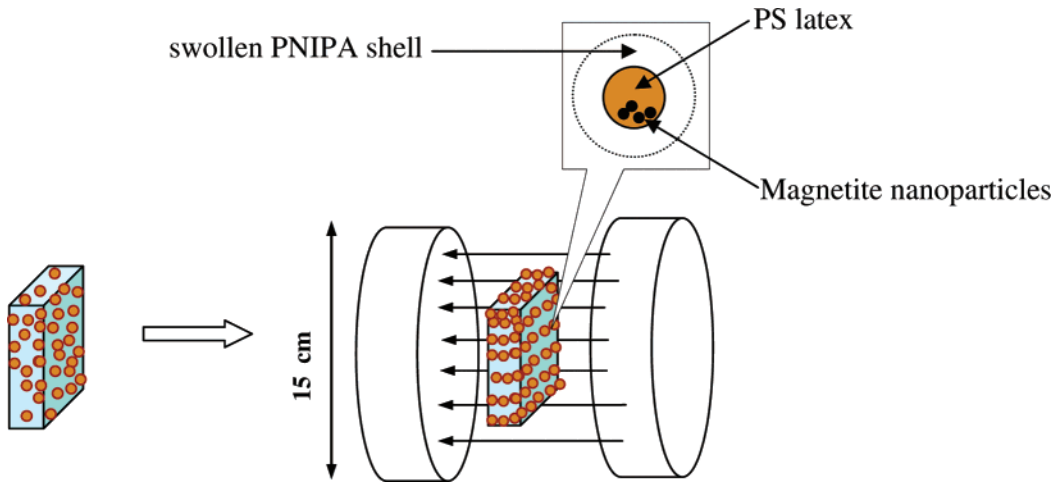

Figure 2. Development and chemical fixation of pearl chain structure of MPS−PNIPA latex particles in PVA gel.

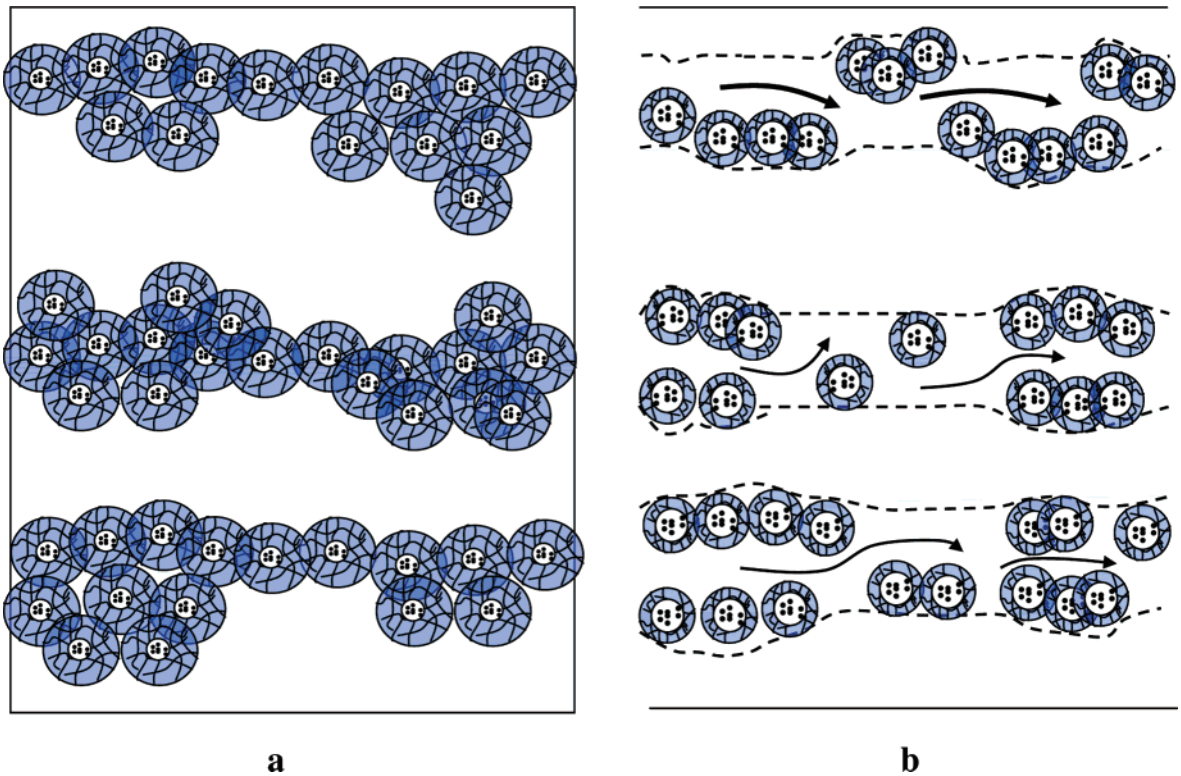

Figure 3. Schematic representation of channels made of MPS−PNIPA latex built in the PVA gel matrix: (a) "off" state below the collapse transition temperature; (b) "on" state above the collapse transition temperature. Arrows indicate the diffusive mass transfer in the channels of PVA membrane.

and PNIPA chains restrict the free movement of the magnetic core−shell beads.

Membrane with Nanoscale Channels as Reversible Molecular Valve That Controls the Permeability. Below the collapse transition temperature the channels in the PVA membranes are fully filled up with MPS−PNIPA latex beads (Figure 3a). As a result, the permeating solute can diffuse only through the PVA and PNIPA hydrogel regions. In this case the diffusivity depends on the volume fraction of the polymer chains in the swollen gel membrane. The polymer chains restrict the mobility of solute molecules, resulting in a small effective diffusion coefficient. When the temperature is increased above the transition temperature, collapse transition of the shell layer of MPS−PNIPA latex takes place, resulting in much smaller bead size. The core−shell beads separate from each other in the gel. Since the bead diameter becomes smaller than that of the channel, the MPS−PNIPA beads no longer fill up the whole space in the channels, and polymer free cavities are formed as shown in Figure 3b schematically. The channels are open, and as a result, the mobility of solute molecules is not restricted by the polymer chains, and so the diffusivity increases. This represents the mechanism of "on/off" switches.

Several attempts have been made in order to detect the MPS−PNIPA channels in the PVA membrane. We have prepared a special membrane in which the thickness of the channels in the swollen state is large enough to be seen by light microscopy. The columnar structure of core−shell beads can be seen in Figure 4.

Permeation Studies. Permeation studies were carried out in a two-compartment diffusion cell. Two chambers are separated by a circular composite membrane having a diameter and thickness of 3.0 and 0.15 cm, respectively. One of the chambers

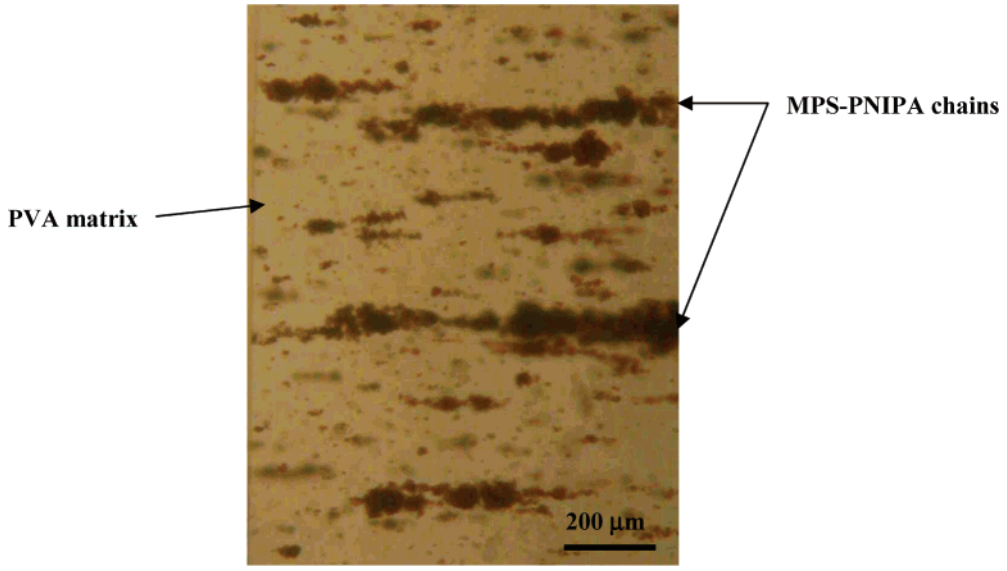

Figure 4. Columnar structure of MPS−PNIPA gel beads in PVA gel membrane seen by light microscope.

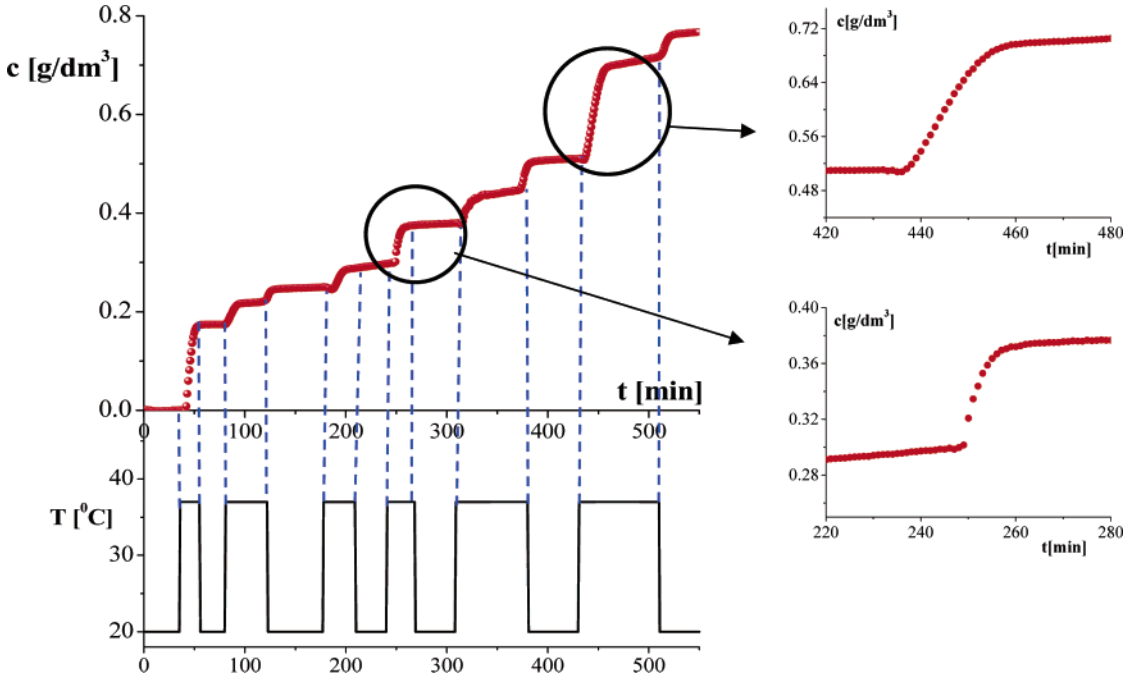

Figure 5. Permeation of bovine serum albumin through PVA membrane in response to stepwise temperature change.

with a volume of 46 cm^3 was filled with the permeant dissolved in distilled water.

Approximate infinite sink condition was maintained by continuously providing the fresh permeant solution to the chamber. The other chamber (42 cm^3), the receptor chamber, was filled with distilled water at the beginning of the experiment, and the permeation was monitored by the spectroscopic method. An Agilent 8453 UV−vis spectrophotometer was used to measure the absorbency as a function of time at a wavelength of 278 nm. To relate the absorbency to the concentration of the permeant, calibration measurements were performed.

Bovine serum albumin (BSA) (Reanal, Hungary) was used as permeate to test the stimuli-responsive nature of the composite membrane. In the studied concentration regime a linear relationship was found between absorbency and concentration: $A = 1.6c$ [g/dm^3].

Figure 5 shows the penetration of BSA through composite PVA membrane responsive to stepwise temperature change between 20 and 37 °C. As the temperature of the solutions surrounding the clamped gel membrane was changed, the permeability changed drastically. With increasing temperature the permeability increased.

This result indicates reversible changes in the permeability upon changes in temperature. An average permeability during each constant temperature interval was calculated on the basis of the cumulative mass of solute permeating into the receptor compartment during that time frame. The "on" permeation value is approximately 1 order of magnitude larger than that permeability in the "off" state. The higher permeation value is due to the collapse of the PNIPA shell in response to temperature change. It is important to mention that the thin PNIPA shell causes the collapse and swelling transition to occur quickly, and the membranes adapt themselves to the new state within a few minutes. Similar permeation patterns were obtained for other permeates like methylene blue and riboflavin with the same membrane.

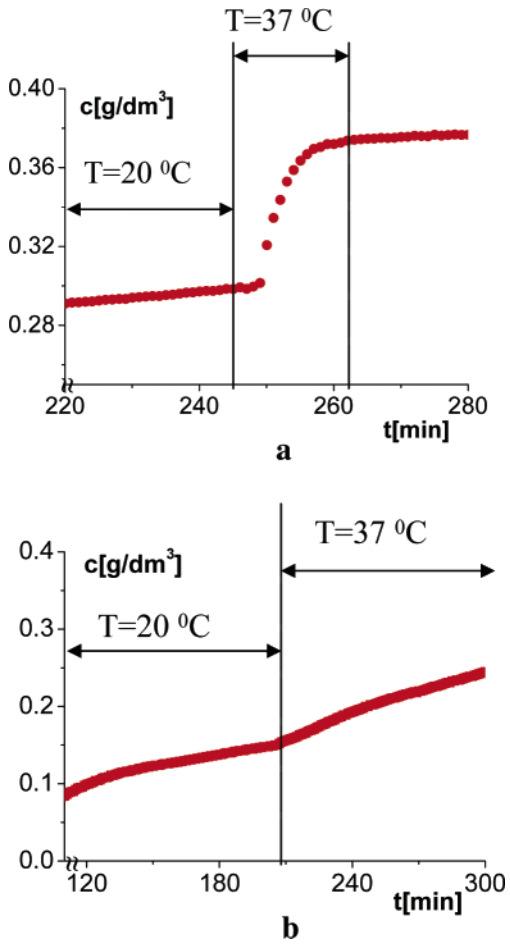

Figure 6. Influence of the spatial distribution MPS−PNIPA beads on the permeation of bovine serum albumin: (a) PVA membrane containing MPS−PNIPA channels; (b) PVA membrane containing randomly distributed MPS−PNIPA beads.

To be sure that the on/off mechanism is due to the channel formation, we have repeated the permeation studies by using randomly distributed MPS−PNIPA beads loaded PVA membrane. The permeation experiment shown in Figure 6b evidences that no on/off mechanism is induced by the stepwise temperature change. This supplementary experiments support the idea that the on/off mechanism is due to the channels formed from MPS−PNIPA core−shell beads.

Conclusions

A new thermoresponsive composite-gel membranes capable of regulating permeability in response to external temperature change has been demonstrated. These membranes containing ordered nanochannels can act as reversible permeability valves. The channels are designed to contain an ordered array of stimuli-responsive core−shell type gel beads that can change their size in response to external stimuli.

This approach is not merely limited to temperature responsive core−shell hydrogels. Through appropriate design the hydrogel shell can sense chemical environments such as pH, specific ions, or molecules and allows self-regulated mass transfer.[6] By varying the thickness of PNIPA shell, it is possible to tune the permeability of the membranes over a wide range.

Since there is a great diversity of external triggers to control the permeability of solutes, this concept could also be used to develop smart membranes whose pores can open and close by electronically induced external triggers such as an electric or magnetic field.

Potential application of specially designed microchannel structures cover a broad spectrum of applications, such as microfiltration, flow control, molecular separation, biomolecule purification, fractionation, and controlled drug delivery. Results of this study would give important information on the matrix design for selective separation of molecules, in particular to those with significant differences in molecular size.

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