PhD theses

Ildikó Csetneki

The relationship between the structures and the properties of colloidal polymer gels

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Introduction and aims

Recently the synthesis and the investigation of polymer gels of colloidal size have attracted particular interest. Several scientists focus their attentions on multifunctional polymer gels, which associate several special properties (magnetic properties, pH- or thermosensitivity), therefore, a variety of stimuli-responsive multifunctional polymer gels have been developed for use in a new, specialized controllable system by external influence (e.g. temperature, pH, electric or magnetic field, etc.).

One of the goals of my PhD work was to synthesize and to characterize nano and microsize beads of temperature, pH, light sensitive properties.

I wanted to prepare stimuli-responsive composite gel membranes containing ordered microchannels. These membranes can act as „on – off switches" or „permeability valves".

The magnetic particles show a random arrangement in the inert polymer matrix when magnetic field is not applied. In uniform magnetic field, however, because of the interaction between the magnetic gels

beads, channel structure made of the pearl-like particles develops. The crosslinking reaction locks the chainlike structure in to the gel, aligned along the direction of the field. The chains of core-shell polystyrene/poly(N-isopropylacrylamide) (MPS/PNIPAAm) particles form channels in the PVA matrix. Below the phase transition temperature the channels in the PVA membranes are fully filled with MPS-PNIPA latex beads. Thus, the PVA and PNIPA hydrogel regions are permeable for the solute molecules. The polymer chains restrict the mobility of the solute molecules. When the temperature is increased above the transition temperature, the channels open, and the mobility of solute molecules is not restricted by the polymer chains.

The permeability and the on-off mechanism of the membrane as a function of the synthesis condition and the environment of the gelbeads. For the membran preparation PNIPAAm, poly(acryl-acid) [PAs], and poly (N' isopropyl-acrylamide)-ko-spirobenzopiran [P(NIPAAm-ko-SP)] latexes were used as the environmental sensitive polymers. The magnetic core and the inert polymer were MPS and PVA, respectively.

Experimental methods

The novel stimuli-responsive membranes, where the permeability can be regulated with a built-in opening-closing mechanism, were investigated using a UV-Vis spectrophotometer (Agilent 8453) as shown in the picture below.

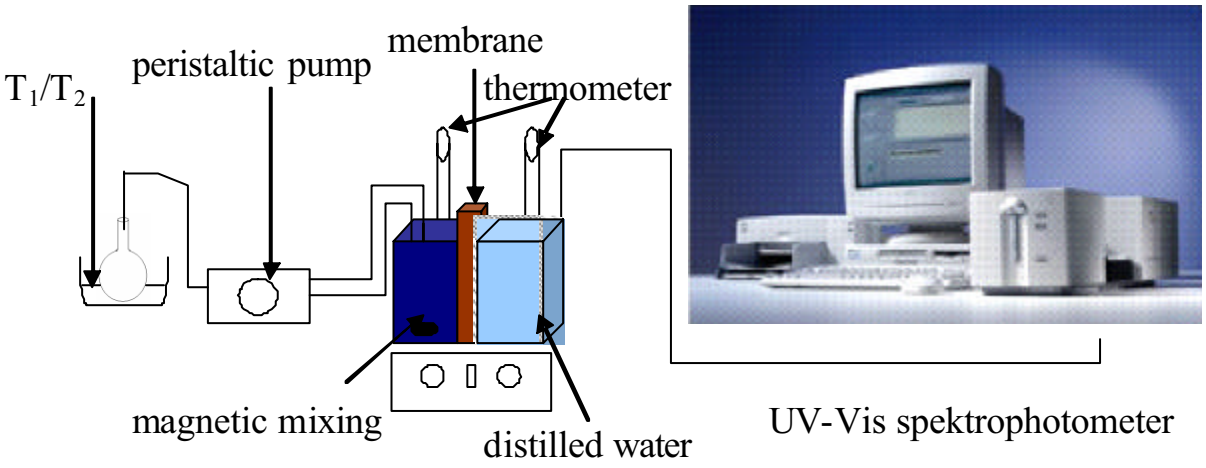

Figure 1: The experiment scheme

The concentration of the sample could be measured on-line using a circulate cuvette and a peristaltic pump; sampling was carried out by the spectrophotometer every minute. The temperature was adjusted and controlled with a heatable magnetic stirrer and ice.

Permeation studies were carried out in a two-compartment diffusion cell (fig.2.) Two chambers are separated by a circular composite membrane. Approximate infinite sink condition was maintained by continuously

stirring both cell compartments. One of the chambers with a volume of 46 cm^3 was filled with the permeant dissolved in distilled water. The fresh permeant solution was added continuously to the chamber. The other chamber (42 cm3), the receptor chamber, was filled with distilled water at the beginning of the experiment.

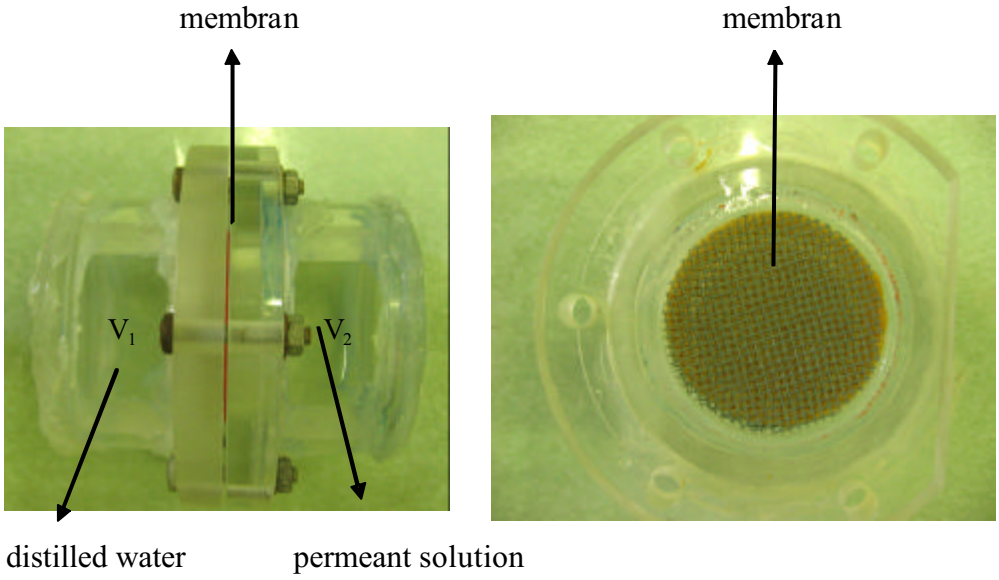

Figure 2: The diffusion cell on the permeation studies

The resulting latexes were characterized with transmission electron microscopy (TEM) and scaning electron microscopy (SEM) measurements. Dynamic light scattering technique and small-angle X-ray scattering was used to measure the size and the distribution of particles. The thermal properties, particularly the temperature induced volume phase transition of the gels were characterized by differential scanning calorimetry (DSC) measurements.

New scientific results

1. Superparamagnetic magnetite particles with an average diameter of 10 nm were built in polystyrene particles by miniemulsion polymerization. The supermagnetic property of the magnetite maintained in the prepared magnetic polystyrene latex (MPS). The colloidal magnetic particles are movable with non-uniform magnetic field. In uniform magnetic field the particles form an aggregated chain-like structure in the direction of the magnetic field.

2. Negative temperature-responsive poly (N' isopropyl-acrylamide) (PNIPAAm) and magnetic poly (N' isopropyl-acrylamide) (MPNIPAAm) latexes were prepared by miniemulsion polymerization.

3. A method was worked out to produce core-shell structured magnetic temperature- and pH-responsive multifunctional latexes. MPS particles (core) were coated by PNIPAAm and poly(acryl-acid) (PAAc) (shell) by core-shell polymerization.

4. A temperature-responsive membrane was prepared by fixing chain-structured MPS- PNIPAAm core-shell composite particles in uniform magnetic field formed in aligned along the direction of the field in a poly(vinyl alcohol) (PVA) matrix.

5. By studying the permeability of the membrane in the function of the temperature of the environment it was found, that increasing the temperature above the phase transition temperature of the PNIPAAm the volume of the core-shell structured gel-spheres are decreasing. The developed channels become permeable for the dissolved molecules. Decreasing the temperature below the phase transition temperature the gel-spheres are swelling, the developed channels close up. It was established that the open-close mechanism of the membrane can be controlled with temperature.

6. The alternation of the membrane permeability was investigated in the function of the thickness of the membrane, the latex content, the extent of the temperature alternation and in the function of the drying procedure. It was found that the optimum of the material

transport is at 1.5mm membrane thickness and 39V/V% latex content. The amount of the transported material was higher by increasing the temperature. The open-close mechanism of the membrane was not influenced by the drying procedure.

7. A pH-responsive membrane was prepared by fixing aggregated in chain-structured MPS/PAAc core-shell composite particles in uniform magnetic field in a PVA matrix.

8. By studying the permeability of the pH-responsive membrane it was found, that in acidic solution the size of the gel-spheres are decreasing. The membrane becomes permeable. In alkaline pH the developed channels close up. It was established that the open-close mechanism of the membrane can be controlled with pH.

9. New type colloidal photo- and temperature-responsive poly (N' isopropyl-acrylamide)-ko-spirobenzopiran [P(NIPAAm-ko-P)] latexes were prepared by miniemulsion polymerization. The results of the investigation by dynamic light scattering show that the

average diameter of the particles before lighting treatment is 300 nm, after the lighting it is 170nm. The photo- and temperature-responsive [P(NIPAAm-ko-P)] particles were fixed in PVA matrix applying polymerization. It was established that the photo- and temperature-responsive property of the particles was retained in the PVA matrix.

Possible technical applications

In the inert polymer matrix, the volume of the nanosized multifunctional gel beads changes rapidly, when only small changes occurs in their environment (changes in temperature, pH, light, etc.).

The size of the pores can be controlled with the diameter and volume changing of individual polymer gel beads.

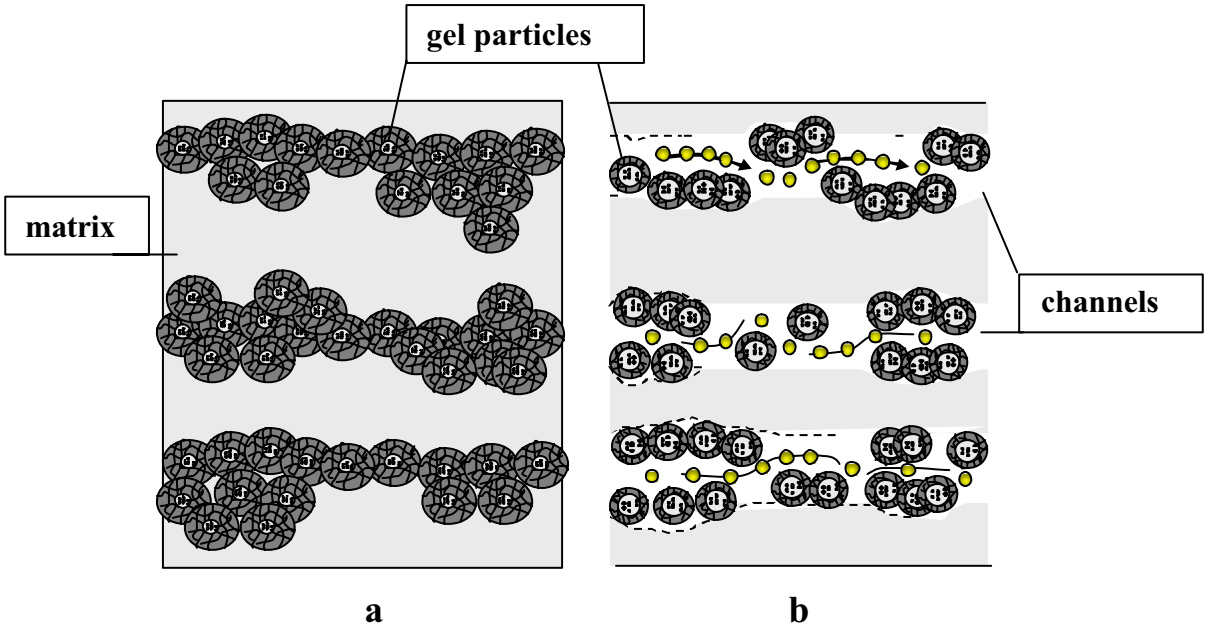

Figure 3: Schematic representation of channels made of MPS/NIPAAm latex built in the PVA gel matrix

a) „off" state below b) „on" state above the collapse transition temperature

It is possible to tune the permeability of the membranes over a wide range. Potential application of the specially designed microchannel structures cover a broad spectrum of applications, such as controlled drug delivery, microfiltration, flow control, molecular separation, biomolecules purification, fractionation.

Publications

1. **I.Csetneki,** M.Kabai Faix, A.Szilágyi, A.L.Kovács, Z.Németh, M.Zrínyi: Preparation of magnetic polystyrene latex via miniemulsion polymerization technique
   Journal of Polymer Science: Part A: Polymer Chemistry, **2004,** 42, 4802-4808. (IF.: 2,773)

2. **I. Csetneki,** G. Filipcsei, M. Zrínyi:
   Smart nanocomposite membranes with controllable permeability
   Macromolecules, **2006,** 39, 1939. (IF.: 3,898)

3. A. Szilágyi, **I. Csetneki,** G. Filipcsei, M. Zrínyi:
   Comparative Study on the Collapse Transition of poly(N-isopropyl acrylamide) Gels and Magnetic poly(N-isopropyl acrylamide) Gels,
   Macromolecular Symposia, **2006**, 239, 130-137. (IF.: 0,895)

4. G. Filipcsei, **I.Csetneki,** A. Szilágyi, M. Zrínyi:
   Magnetic Field-responsive Smart Polymer Composites
   Advances in Polymer Science, accepted, **2006.** (IF.: 7,320)

5. M. Zrínyi, **I. Csetneki,** G.Filipcsei, Cs. Simon, J. Gács:
   Szabályozható permeabilitású membrán kontrollálható nyitó-záró mechanizmussal (és szelektivitással) Hungarian Patent P0600038 **2006.**01.18.

Related papers:

6. **Csetneki I.,** Filipcsei G., Zrínyi M.:
   Polimergélek duzzadásának mechanizmusa, termodinamikája és kinetikája
   Magyar Kémiai Folyóirat, **2002,** 108, 3. (IF.: 0,207)

7. T. Hajsz, **I. Csetneki,** G. Filipcsei, M. Zrínyi:
   Swelling Kinetics of Anisotropic Filler Loaded PDMS networks
   Physical Chemistry Chemical Physics, **2006,** 8, 1-8. (IF.: 2,076)

Oral presentation:

1. **Csetneki Ildikó:** Szabályozható permeábilitású membrán kontrollálható nyitó-záró mechanizmussal
   Vegyészmérnöki Kar 3. doktoráns konferencia,
   2006.02.07.