論文題目 　　　Stimuli-responsive mesoporous membranes using block copolymer
（ブロックコポリマーを用いた刺激応答性メゾポーラス膜）

氏　　　名　　　唐 彦春

Stimuli-responsive membranes which can change their chemical, physical and barrier properties by responding to the environmental conditions have attracted large attention and shown tremendous development in last two decades. Different types of stimuli were applied to induce responses, including the direct stimulants such as temperature, pH, specific ions, and newly emerged remote triggers such as light, electric and magnetic fields. The existing stimuli-responsive membranes are often prepared by surface modified commercial template membranes with stimuli-responsive polymers using the "grafting to" and "grafting from" approaches. Because the diffusion of the polymer chains or monomers into membrane pores is prevented by already grafted brushes and narrow pore walls, those approaches are with inherent difficulties to prepare stimuli-responsive membranes with pore size lower than 100 nm.[1]

In this study, by using amphiphilic block copolymers (BCPs) as templates, three kinds of stimuli-responsive mesoporous membranes with excellent and unique responsivity have been developed. The first type is **thermo-responsive mesoporous block copolymer membrane** prepared by introducing nanopores into poly(oligoethylene glycol methyl ether methacrylate)-*b*-polystyrene-*b*-poly(oligoethylene glycol methyl ether methacrylate) ($PMEO_nMA$-*b*-PS-*b*-$PMEO_nMA$) templates via selective swelling the $PMEO_nMA$ domains. The membrane with PS being the mechanical stable part of the matrix and thermo-responsive $PMEO_nMA$ covered the mesopores interiors. The lower critical solution temperature (LCST) of $PMEO_nMA$ is tunable by changing the average number of ethylene glycol repeating units in the side group, n, thus providing the membrane a tuning the thermos-responsivity.[2] The second type is **magneto-responsive mesoporous block copolymer membrane** constructed by embedding iron oxide nanoparticles (IONPs) as local heaters into the PS matrix of the foresaid porous block copolymer membrane. The swollen/shrunken state of $PMEO_nMA$ brushes on the pore walls can be triggered by the heat generation of nearby IONPs, therefore the molecular sieving performance of the membrane can be adjusted.[3] The third type is **thermo-and pH-responsive mesoporous block copolymer membrane** fabricated with poly(N,N-dimethylaminoethyl methacrylate)-*b*-poly(diethyleneglycol methyl ether methacrylate)-*b*-polystyrene (PDMAEMA-*b*-$PMEO_2MA$-*b*-PS) by selective swelling PDMAEMA-b-$PMEO_2MA$ domains. $PMEO_2MA$ has LCST at 26 °C. PDMAEMA is a typical weak polyelectrolyte with pK_a value at 7.0-7.5 and also a thermo-responsive polymer revealed a LCST of 20-80 °C in aqueous solution. With combination of the properties of $PMEO_2MA$ and PDMAEMA, such membrane pore size can be varied into 4 different barrier dimension as function of the combination of temperature and pH.

1. **Thermo-responsive mesoporous block copolymer membranes**

Three ABA type block copolymers---PMEO$_2$MA-*b*-PS-*b*-PMEO$_2$MA, PMEO$_{2.2}$MA-*b*-PS-*b*-PMEO$_{2.2}$MA, and PMEO$_3$MA-*b*-PS-*b*-PMEO$_3$MA---were chosen as BCP templates. All of them have very high molecular weight (120-150 kDa) and the PMEO$_n$MA/PS ratio was 30/70. The membranes were with double layer structure having a mesoporous size-selective BCP layer on the top of a polyvinylidene fluoride (PVDF) macroporous supporting layer (Figure 1a). Bicontinuous porous structure was formed over the entire BCP layers, with a narrow pore-size distribution around 50 nm in dry state. The formation of porous structure is attributed to methanol-scCO$_2$ (super critical CO$_2$) selective swelling method which is outlined in Scheme 1. Methanol-scCO$_2$ system can form a homogeneous phase above the vapor-liquid equilibrium line. After the self-assembled PMEO$_n$MA-*b*-PS-*b*-PMEO$_n$MA coated membranes immersed in Methanol-scCO$_2$ system, scCO$_2$ effectively plasticizes the PS matrix and methanol diffuse into PMEO$_n$MA domains. Due to the swelling induced volume expansion, the PMEO$_n$MA domains fuse with neighboring domains, forming a continuous phase (Scheme 1b). Upon depressurization, the methanol-scCO$_2$ system phase separates, and the CO$_2$ is removed from the PS matrix. The PS domains become glassy, maintaining the polymer structure, while PMEO$_n$MA domains remain swollen with methanol. After drying, the swollen PMEO$_n$MA blocks fixed on the solid PS walls release methanol and shrink. Consequently, bicontinuous mesopores are introduced and the pore walls are covered with PMEO$_n$MA chains (Scheme 1c).[4, 5]

Water permeability results showed that the pore size increased gradually until the temperature reached the response temperature of each membrane ranging from 20°C to 50°C (Figure 1b). It indicates the thermo-responsive brushes were formed inside the pores and membranes possess tunable response temperature. These membranes are promising for separating nanoparticles. For the membranes fabricated from PMEO$_2$MA -*b*-PS-*b*- PMEO$_2$MA, the rejection rate of 5 nm colloidal gold particles decreased from 88% at 10°C to 10% at 40°C, and the rejection rate of 15 nm colloidal gold particles was 100% even at 40°C.
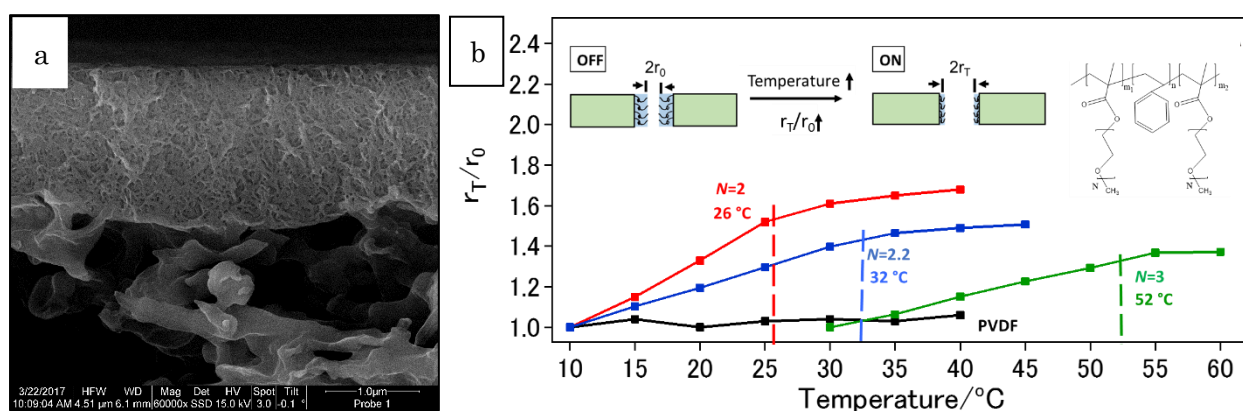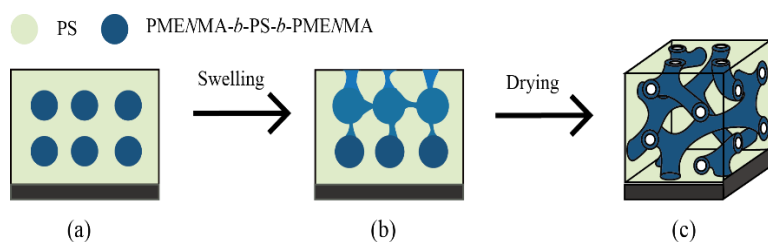

Figure 1. SEM images of (a) cross-section of PMEO$_{2.2}$MA-*b*-PS-*b*-PMEO$_{2.2}$MA and (b) Relative pore radius (r_T/r_0) for 220 nm PVDF base membrane and PMEO$_n$MA-*b*-PS-*b*-PMEO$_n$MA composite membranes.

Scheme 1. Schematic depiction for the Methnol-scCO$_2$ selective swelling method.

2. Magneto-responsive mesoporous block copolymer membranes

Mesoporous magneto-responsive membranes were composed a thin mesoporous size-selective layer containing IONPs embedded in PMEO$_{2.2}$MA-b-PS-b-PMEO$_{2.2}$MA, on top of a PVDF macroporous support membrane. IONPs and PMEO$_{2.2}$MA-b-PS-b-PMEO$_{2.2}$MA mixture solutions were spun-cast on PVDF membranes, and then mesopores were introduced into the hydrophilic PMEO$_{2.2}$MA domains by controlled selective swelling with methanol-scCO$_2$ system. The loaded IONPs aggregated into small clusters (0.1-1 µm) and were finely dispersed in the PMEO$_{2.2}$MA-b-PS-b-PMEO$_{2.2}$MA mesoporous top layer. Their barrier pore sizes were almost identical to those of no IONPs containing membranes and no defect was found, as shown in Figure 3a.

Upon stimulation with alternating magnetic field with different input energy, the water permeability as well as the dextran rejection were tuned into different levels, indicating that the sieving barrier pore size distribution of these thin-film mixed matrix nanocomposite membranes was step-wise adjustable (Figure 3b).
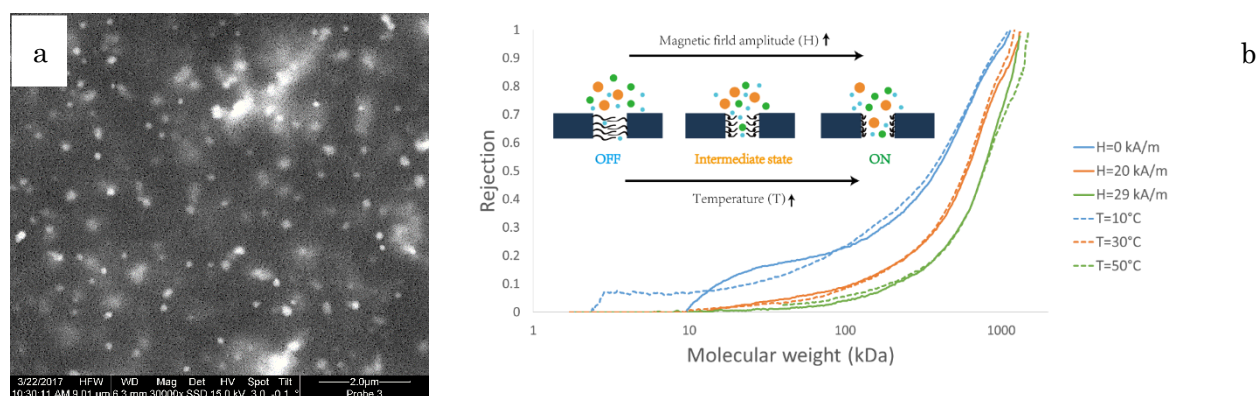

Figure 3. (a) SEM images of top view of magneto-responsive membrane. (b) Rejection coefficients as a function of dextran molecular weight of the magneto-responsive membranes with AMF at different magnetic field amplitude (0, 20 and 29 kA/m, feed temperature fixed at ~15°C) and at different temperature (10 °C, 30 °C and 50 °C).

3. Thermo- and pH-responsive mesoporous block copolymer membrane

The double-responsive membranes were prepared with PDMAEMA-b-PMEO$_2$MA-b-PS (PDMS) tri-block copolymer using the methanol-scCO$_2$ selective swelling method. Scanning electron microscopy (SEM) probed successful introduction of mesopores into BCP films and pore size was narrowly distributed. With permeability measurements with different feed and temperature, we found the PDMS membrane had a combination of the

properties of PDMAEMA-*b*- PS (PDS) and PMEO₂MA-*b*-PS (PMS) membranes, with two-step thermo-responsivity ($LCST_{PMEO2MA}$= 26°C, $LCST_{PDMAEMA}$ = 40°C) and also reversibly changing ultrafiltration properties with independent response to temperature and pH (Figure 4a). It indicates that the PDMAEMA-*b*-PMEO₂MA chains attached on the interiors of mesopores of BCP barrier layer, and an expanded or collapsed state for each of the individual blocks was obtained. Further, we also tried to investigate the conformation transition of PDMAEMA-*b*-PMEO₂MA brush depending on temperature with neutron reflectometry, this work is partially done.
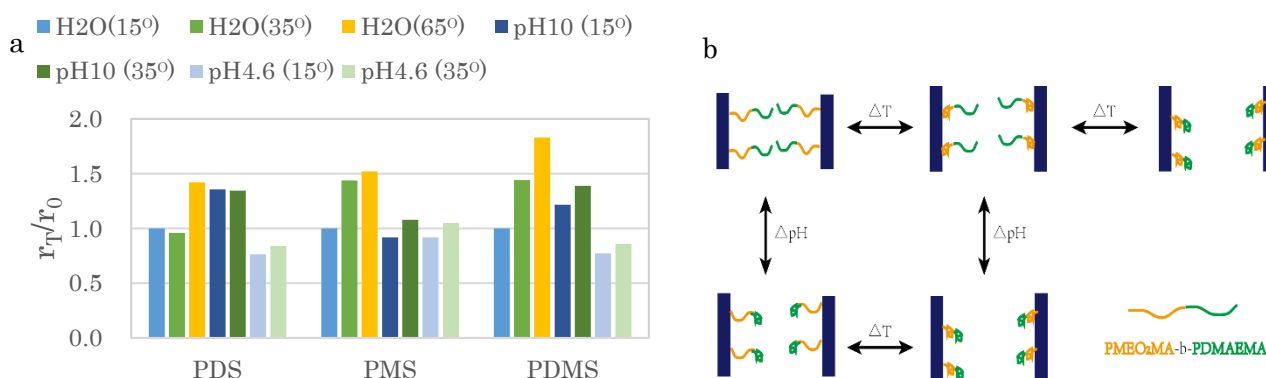

Figure 4. (a) The relative pore radius (r_T/r_0) for PDS, PMS and PDMS membranes, calculated from permeability data measured with water, carbonate buffer (pH=10.1) and acetate buffer (pH=4.6) at different temperature. (b) Schematic illustration of 4 different chain expansion states in dependency of pH and temperature lead to 4 different pore sizes. For PDMS membrane, PMEO₂MA blocks are in the "inner" layer and PDMAEMA blocks in the "outer" layer.

4. References

1.	Wandera, D.; Wickramasinghe, S. R.; Husson, S. M. Stimuli-responsive membranes. *Journal of Membrane Science* **2010,** 357 (1), 6-35.

2.	Tang, Y. C.; Ito, K.; Hong, L.; Ishizone, T.; Yokoyama, H. Tunable Thermoresponsive Mesoporous Block Copolymer Membranes. *Macromolecules* **2016,** 49 (20), 7886-7896.

3.	Tang, Y.; Lin, X.; Ito, K.; Hong, L.; Ishizone, T.; Yokoyama, H.; Ulbricht, M. Tunable magneto-responsive mesoporous block copolymer membranes. *Journal of Membrane Science* **2017,** 544 (Supplement C), 406-415.

4.	Zhang, R.; Yokoyama, H. Fabrication of Nanoporous Structures in Block Copolymer Using Selective Solvent Assisted with Compressed Carbon Dioxide. *Macromolecules* **2009,** 42 (10), 3559-3564.

5.	Gong, J. L.; Zhang, A. J.; Bai, H.; Zhang, Q. K.; Du, C.; Li, L.; Hong, Y. Z.; Li, J. Formation of nanoscale networks: selectively swelling amphiphilic block copolymers with CO2-expanded liquids. *Nanoscale* **2013,** 5 (3), 1195-1204.