

## Micro- and Nano-Fabrication of Stimuli-Responsive Polymers

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Various types of stimuli-responsive polymers have been designed and synthesized. The polymers, almost always polyelectrolytes, undergo abrupt changes in conformation, optical properties, volume, and so on in response to external stimuli such as pH, temperature, ions, solvent components, electric field, chemical reactant, and light irradiation. The responsiveness is attributed to the ionic groups in the polymers, which are reversibly deionized in response to the stimuli. The ionic state significantly affects the polymer conformation, which results in drastic changes in the physical properties. The stimuli-responsive polymers have been investigated by many researchers to construct intelligent or smart materials (1).

We have devised some micro- or nano-fabrication method using stimuli-responsive polymers. One was photolithographic synthesis of micro-gels. Poly(acrylic acid) or poly(N-isopropylacrylamide-co-acrylic acid) was chosen as a pH- or a thermo-responsive polymer, respectively, and the polymer was modified with azidophenyl groups to be a photo-reactive polymer. The modified polymer was cross-linked in the presence of photo-masks as shown in Figure 1. When the crosslinking reaction occurred on the polystyrene plate, the formed gel was immobilized on the surface. On the other hand, on the glass plate the formed gel was removed from it. The shapes of removed microgels spontaneously changed in response to stimulus as shown in Figure 2.

Another was carried out by grafting the pH or thermo-responsive polymer on nanoporous filter membranes. Figure 3 shows some method to graft polymers on surfaces.

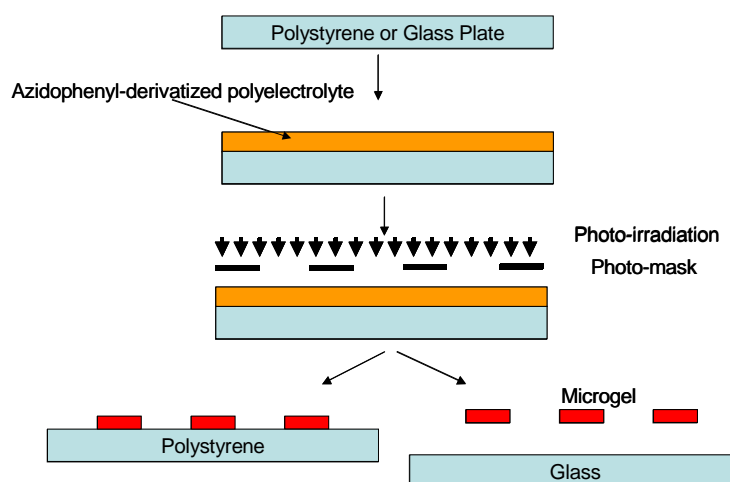


Figure 1 Preparation of stimuli-responsive gels on polystyrene or glass plate.

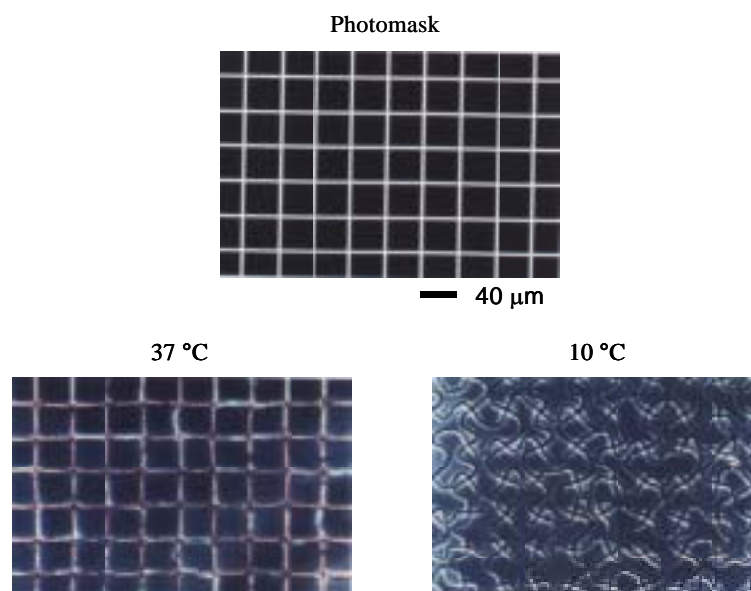


Figure 2 Microgel was formed by the above photo-mask responded to temperature. At 37oC the microgel shrank and at 10oC the microgel swelled to form a unique structure. The change was reversible.

“Grafting from” is graft-polymerization on surfaces. On the other hand, “grafting to” means immobilization of polymer on surfaces. End-on grafting uses reactive end group in the polymer and side-on grafting employs reactive side groups in the polymer. The stimuli-responsive polymers were grafted on porous membranes by these methods. The conformational change of grafted polymers in response to stimulation induced size change of nanopores of the membrane and as a result substance permeation through the membrane was regulated. Figure 4 shows the self-assembly of poly(acrylic acid) carrying thiol groups in the side chains on gold-coated porous membrane as the example. At low pH the polymer shrank to open the nanopore and at high pH it extended to close the pore. The open of nanopores enhanced the substance permeation and the closing reduced it. This size change was observed by atomic force microscopy in water.

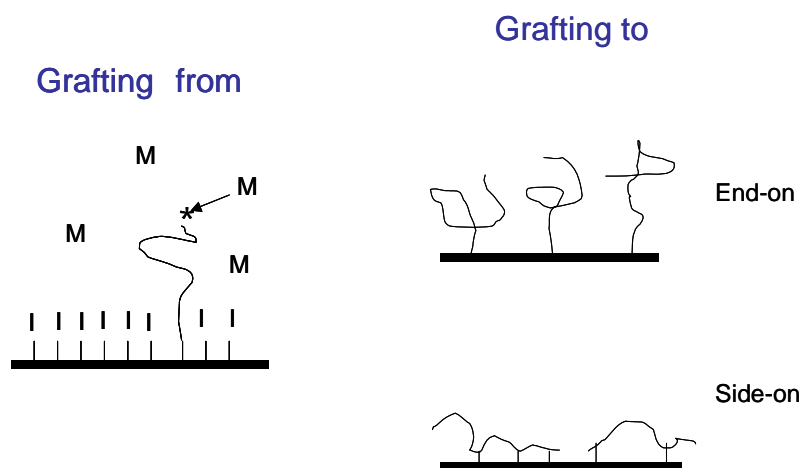


Figure 3 Classification of grafting methods M and I mean monomer and initiator, respectively.

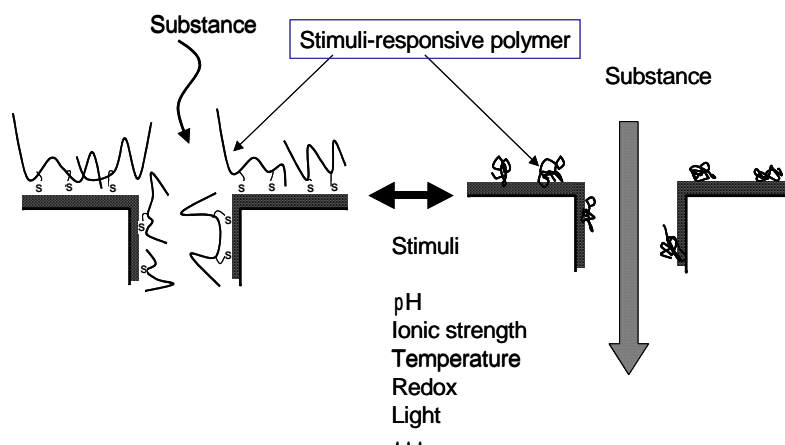


Figure 4 Stimuli-responsive permeation of substances through stimuli-responsive polymer-grafted porous membrane.

These fabrication methods will be useful for construction of smart micro- or nano-devices in the future.

References

1.H. Zhang and Y. Ito, “Smart materials using signal-responsive polyelectrolytes,” in “Handbook of polyelectrolytes and their applications” ed. by S. K. Tripathy, J. Kumar, and H. S. Nalwa, American Scientific Pub., 2002, p.183-206

# Micro- and Nano-Fabrication of Stimuli-Responsive Polymers

Kanagawa Academy of Science  
and Technology  
Yoshihiro Ito

# Signal-Responsive Polymers



pH

Ion

Oxidation

Temperature

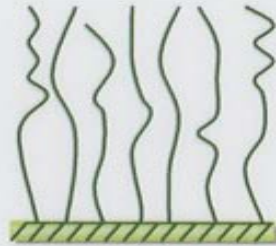
Photo-Irradiation

Glucose

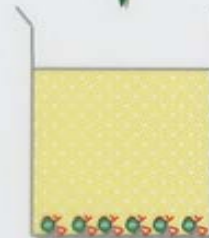
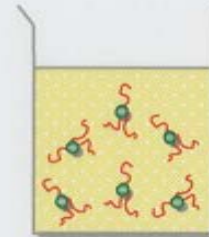
# Smart materials



Hydrogels



Surfaces



Solutions

# Systems using stimuli-responsive polymers

Regulation of soluble and insoluble states

- Nano-fusion

Regulation of extension of polymer chain

- Surface modification

Swelling and shrinkage of polymeric gels

- Photo-lithography

# Stimuli-responsive polymer

Enzyme



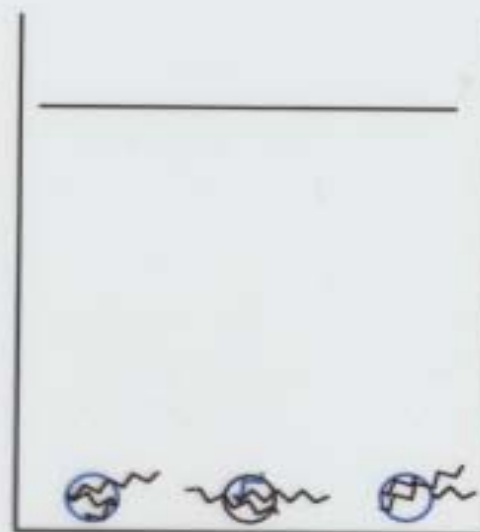
pH

Temperature

Ion

Redox

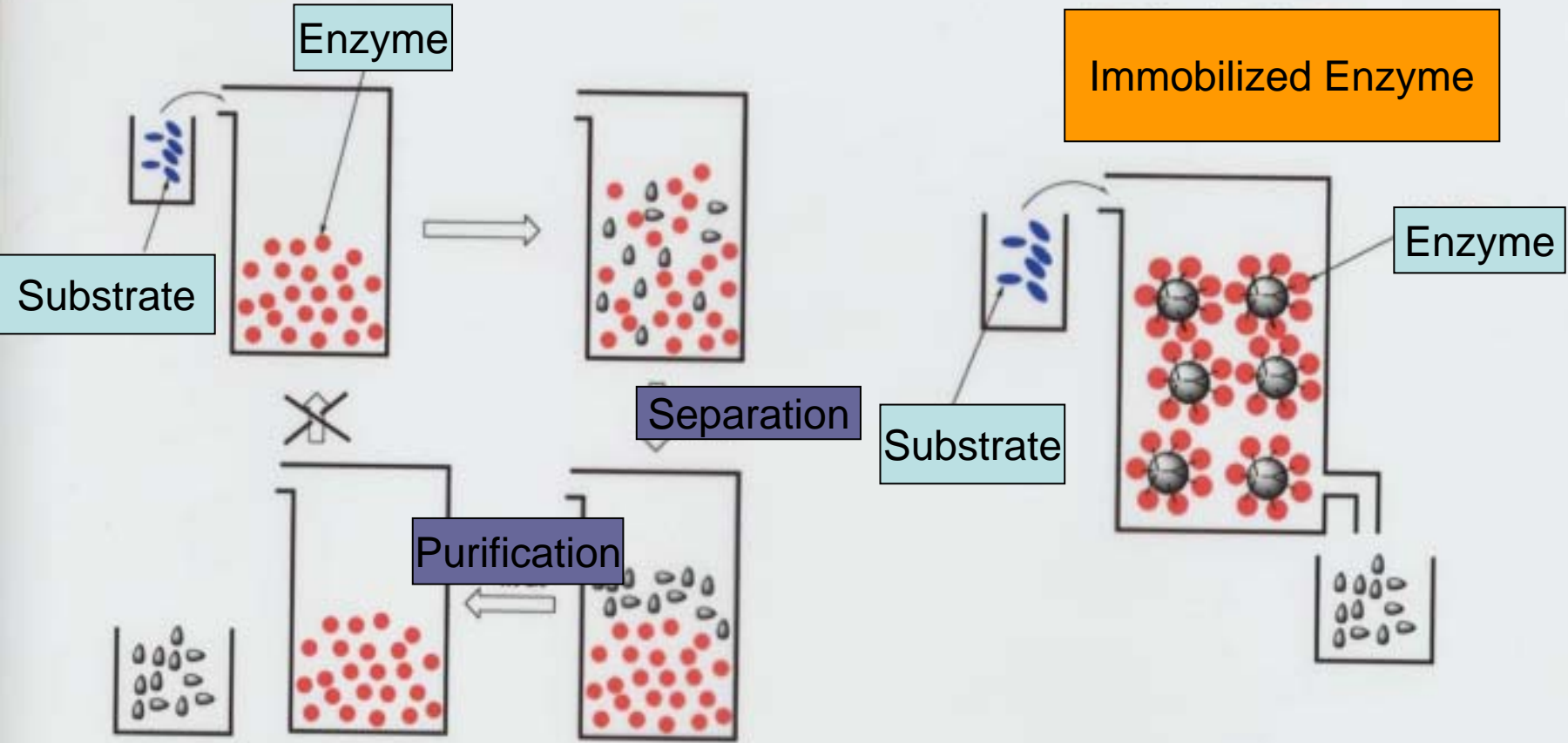
Photo

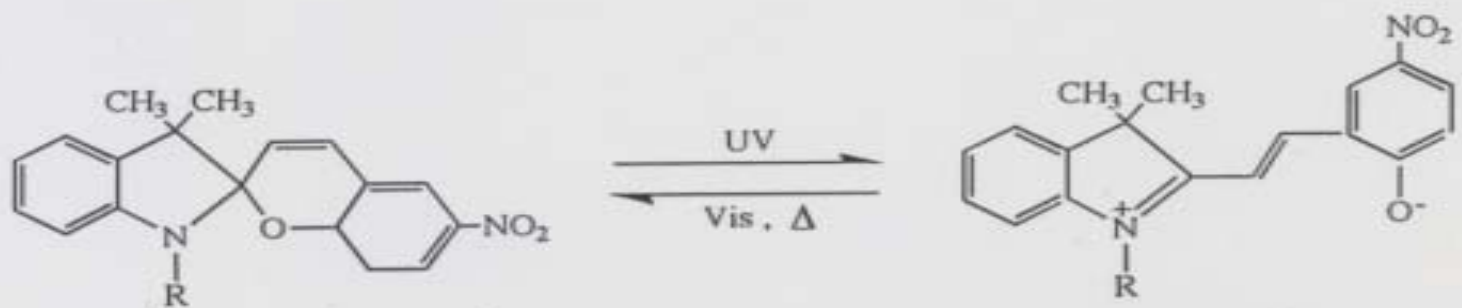


Soluble  
Active

Precipitate  
Inactive

# Bioractor

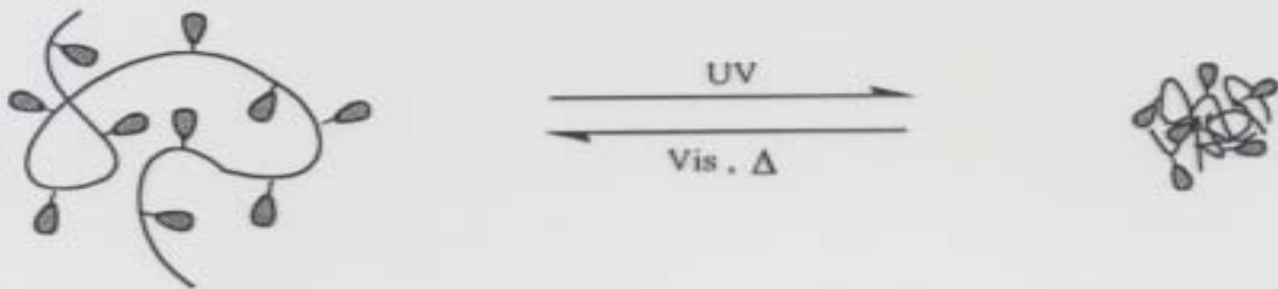




Spiropyran-form

Merocyanine-form

Photoisomerization of spiropyran



Polymer-solvent  
interaction

Polymer-polymer  
interaction

A



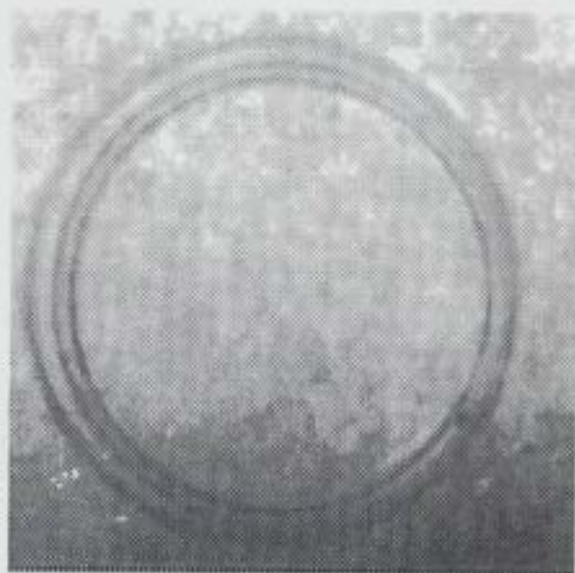
B



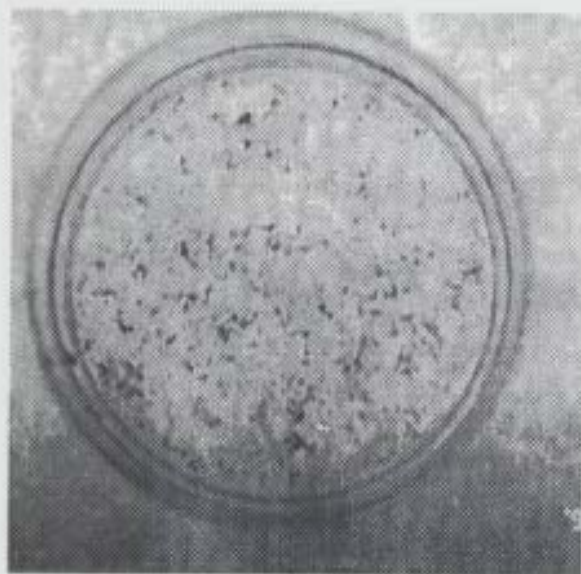
C

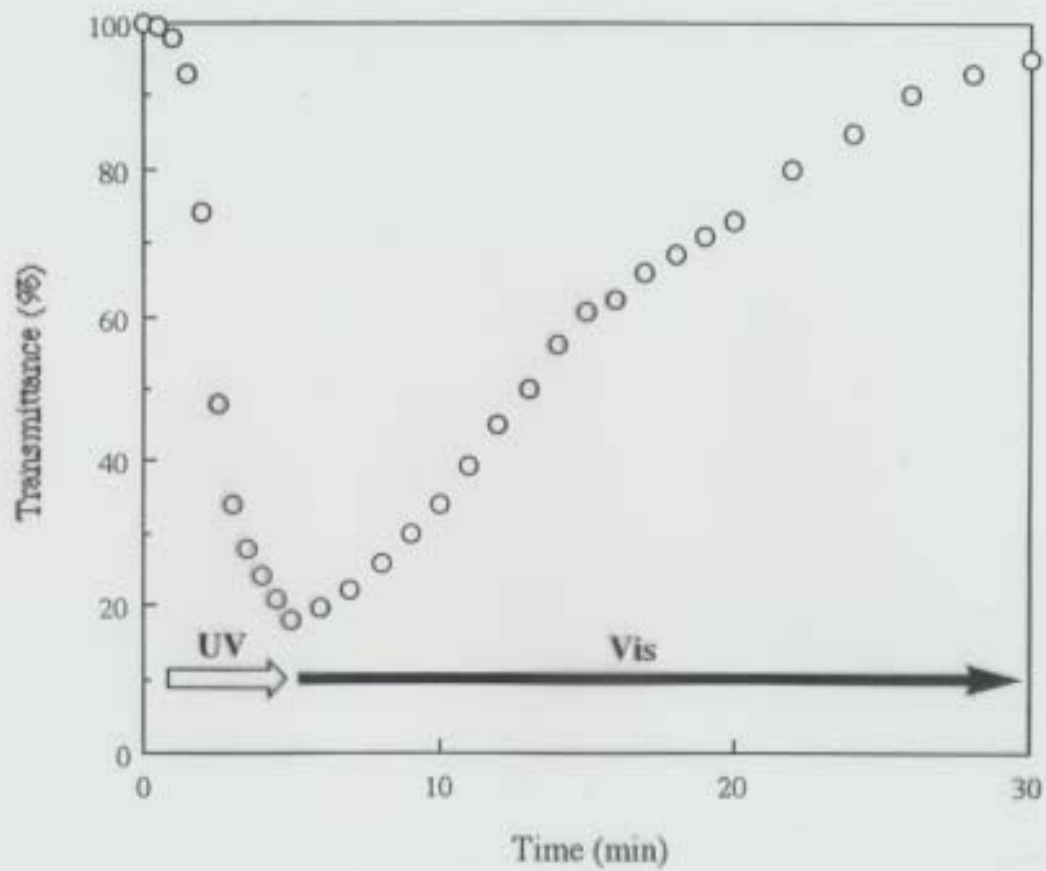


b



UV  
Vis





Stimuli-responsive polymer

Enzyme

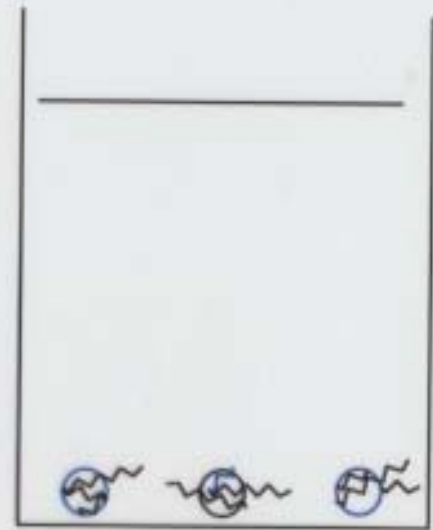
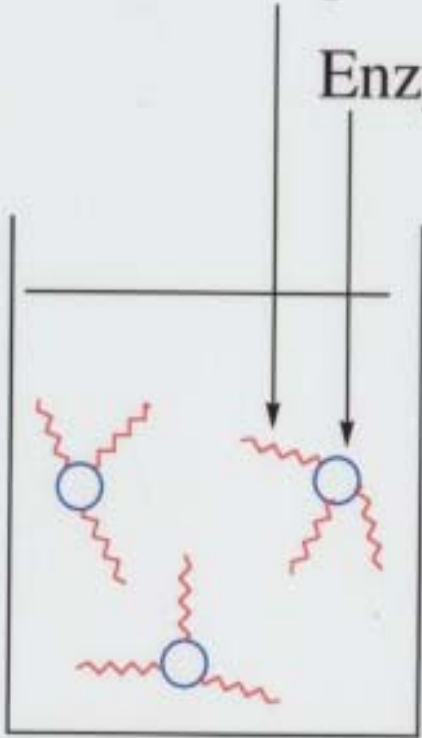
pH

Temperature

Ion

Redox

Photo



Soluble  
Active

Precipitate  
Inactive

# Systems using stimuli-responsive polymers

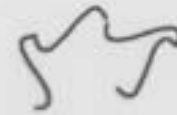
Regulation of soluble and insoluble states

Regulation of extension of polymer chain

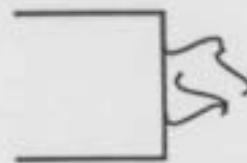
Swelling and shrinkage of polymeric gels



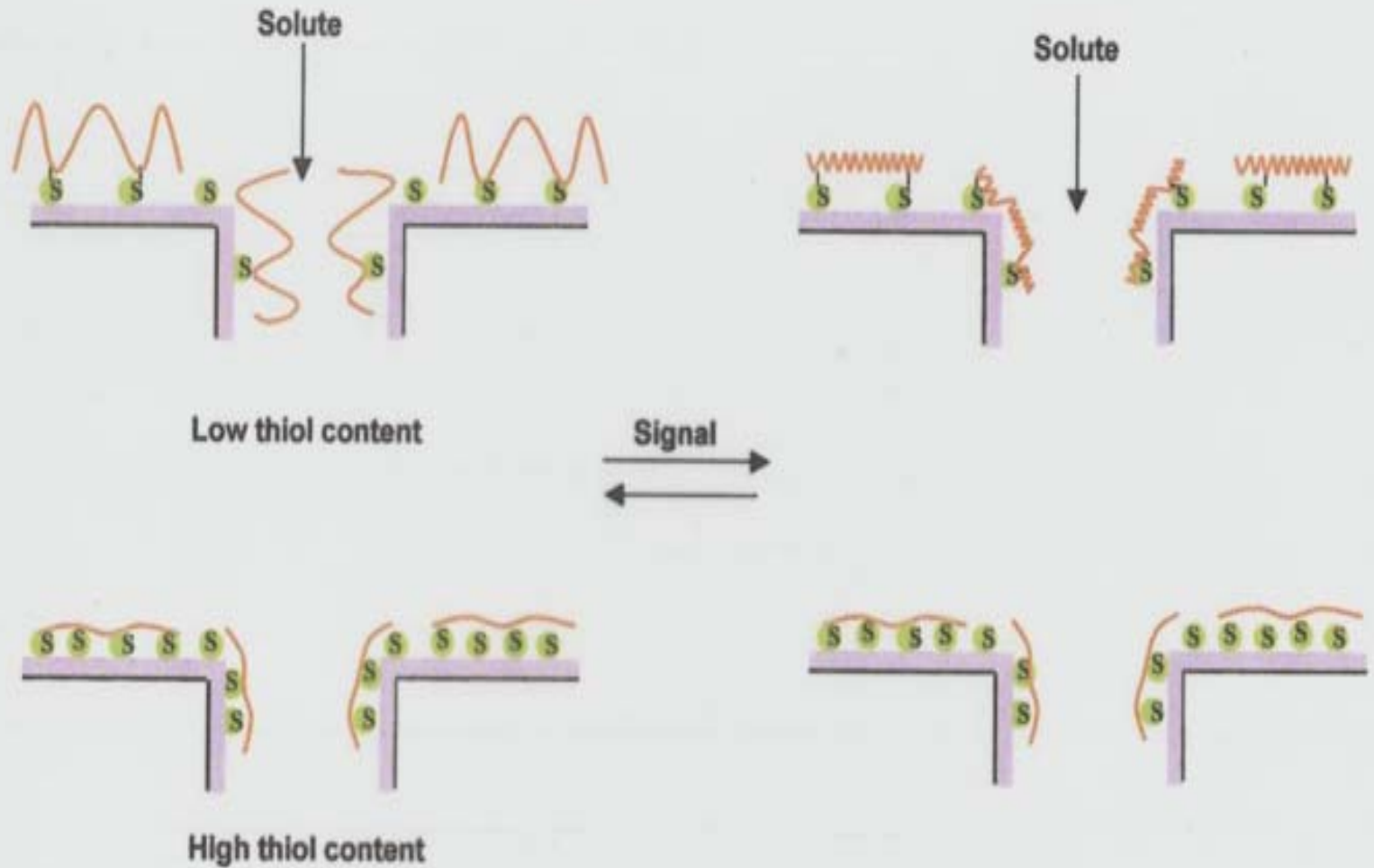
Stimulation



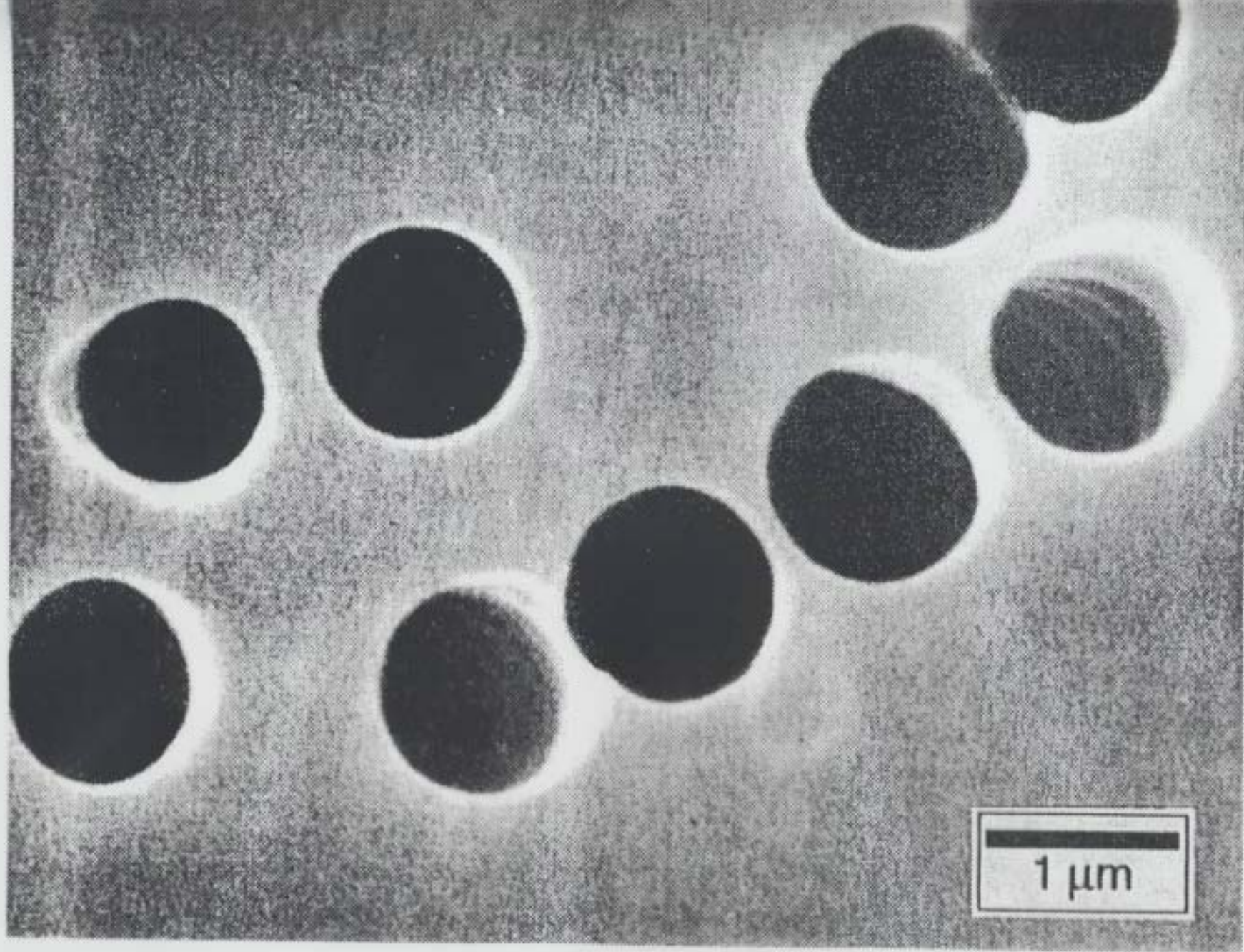
Stimulation



**Substance Permeation**



**Schematic illustration of regulating the solute permeation through the PAA-HS self-assembled membrane.**

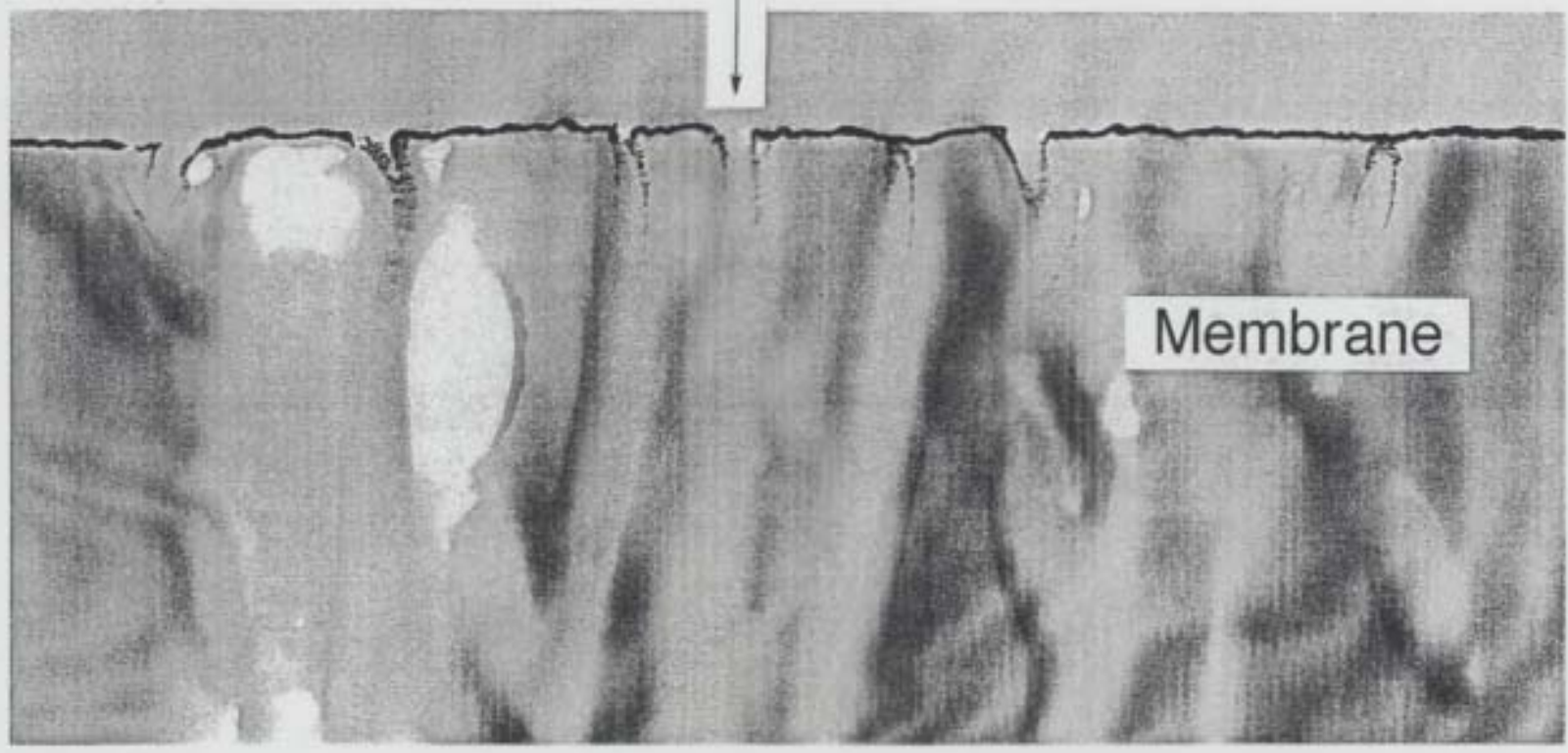


1 μm

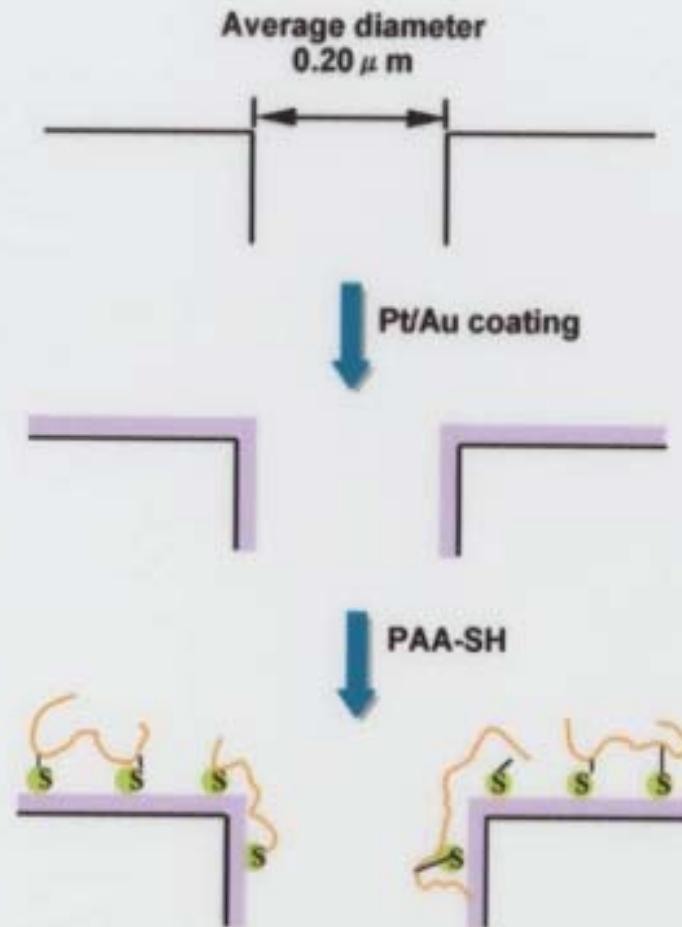


Pore

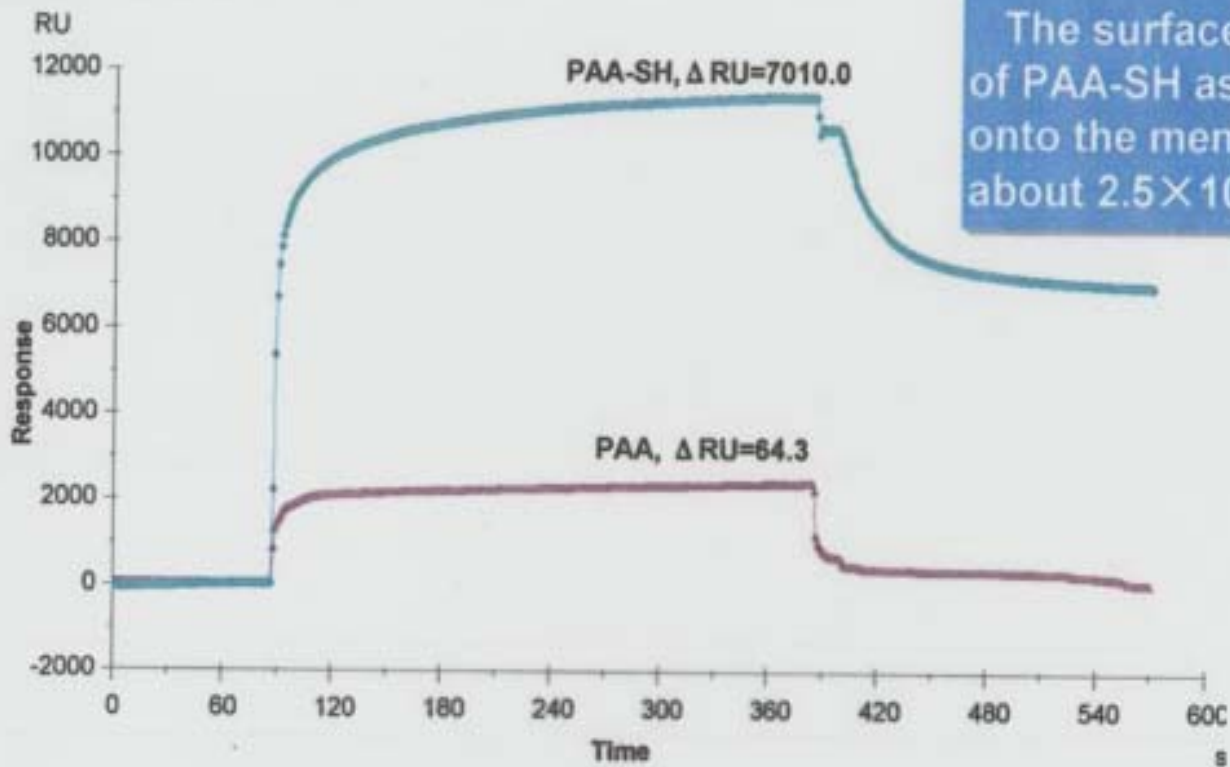
— 500 nm



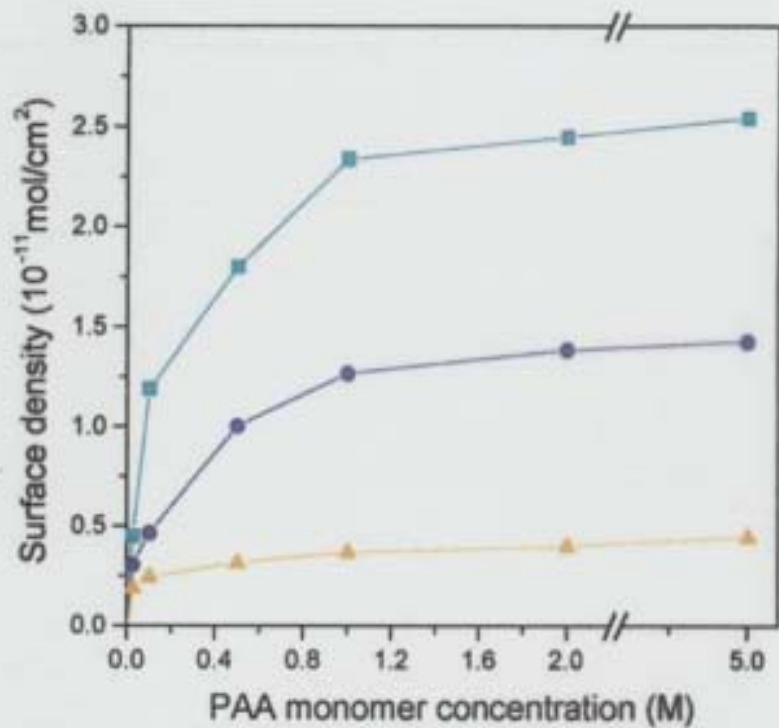
Membrane



Preparation scheme of signal-responsive gating by modified PAA on a nanoporous membrane

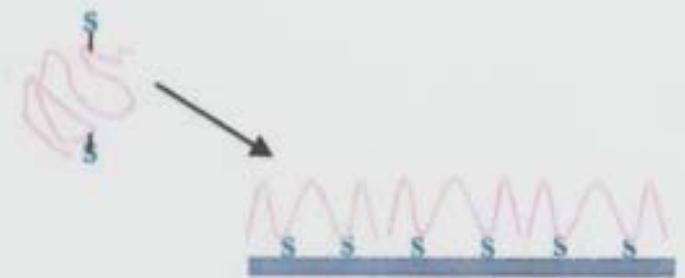


Surface plasmon resonance (SPR) spectra showing the binding of thiol group to a Au-coated plate. Significant binding of the modified PAA with HS-Au bound occurred, whereas very little binding occurred for PAA.



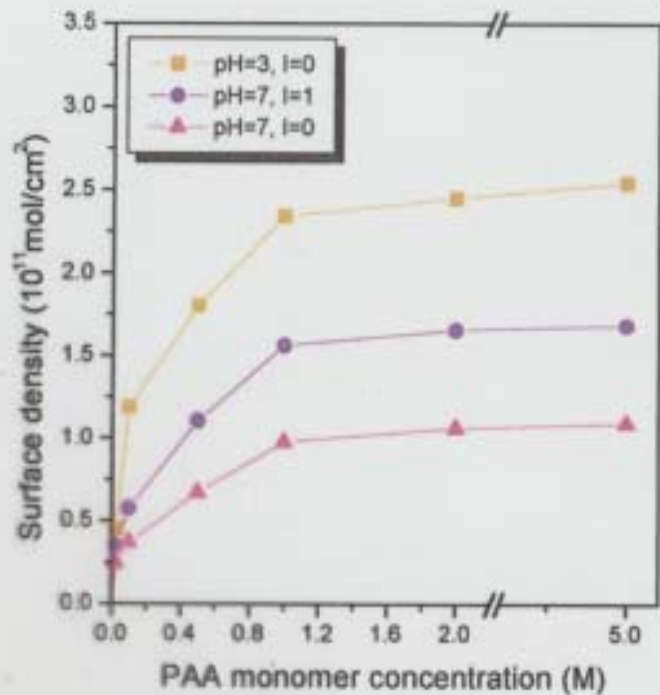
**Surface density vs. the concentration of solution for PAA-HS with thiol content of 2(■), 10(●) and 30(▲) thiols / 100 carboxyls.**

**Lower thiol content**

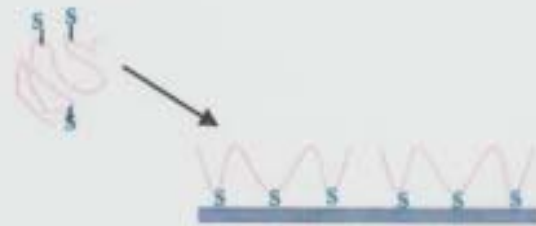


**Higher thiol content**





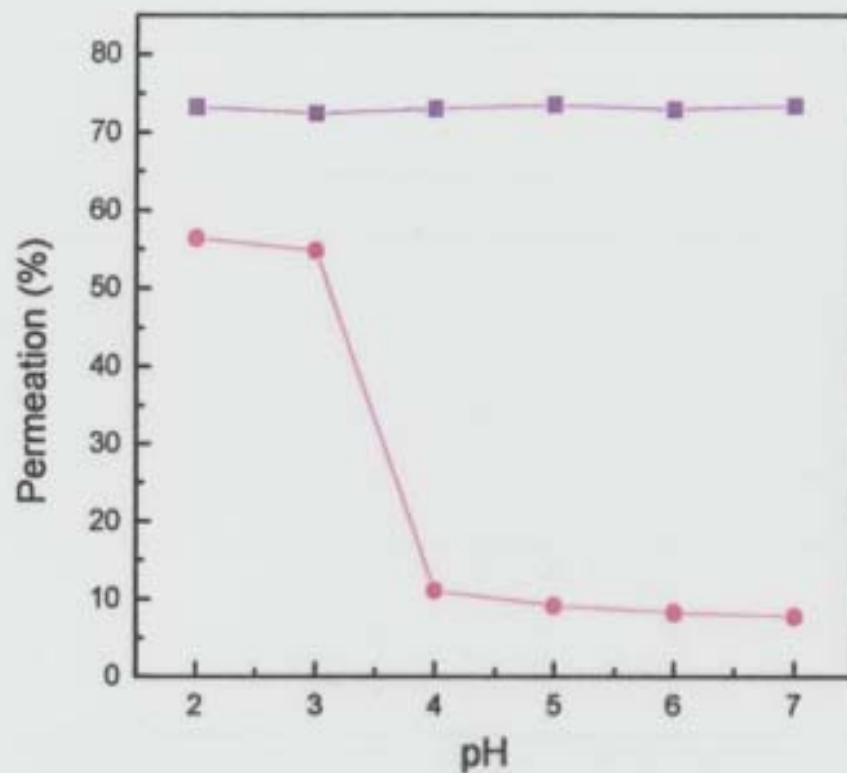
Lower pH or higher ionic strength



Higher pH or lower ionic strength



The effects of pH and ionic strength on the self-assembly of PAA-SH.

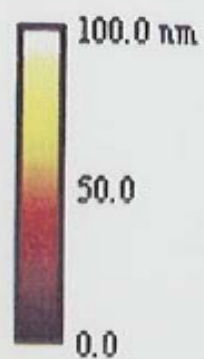


**pH dependence of water permeation for bare membrane (■) and membrane immobilized with PAA-SH (●). Thiol content was 2 thiols / 100 carboxyls and surface density was  $1.8 \times 10^{-11} \text{ mol/cm}^2$ .**

**pH 3.0**

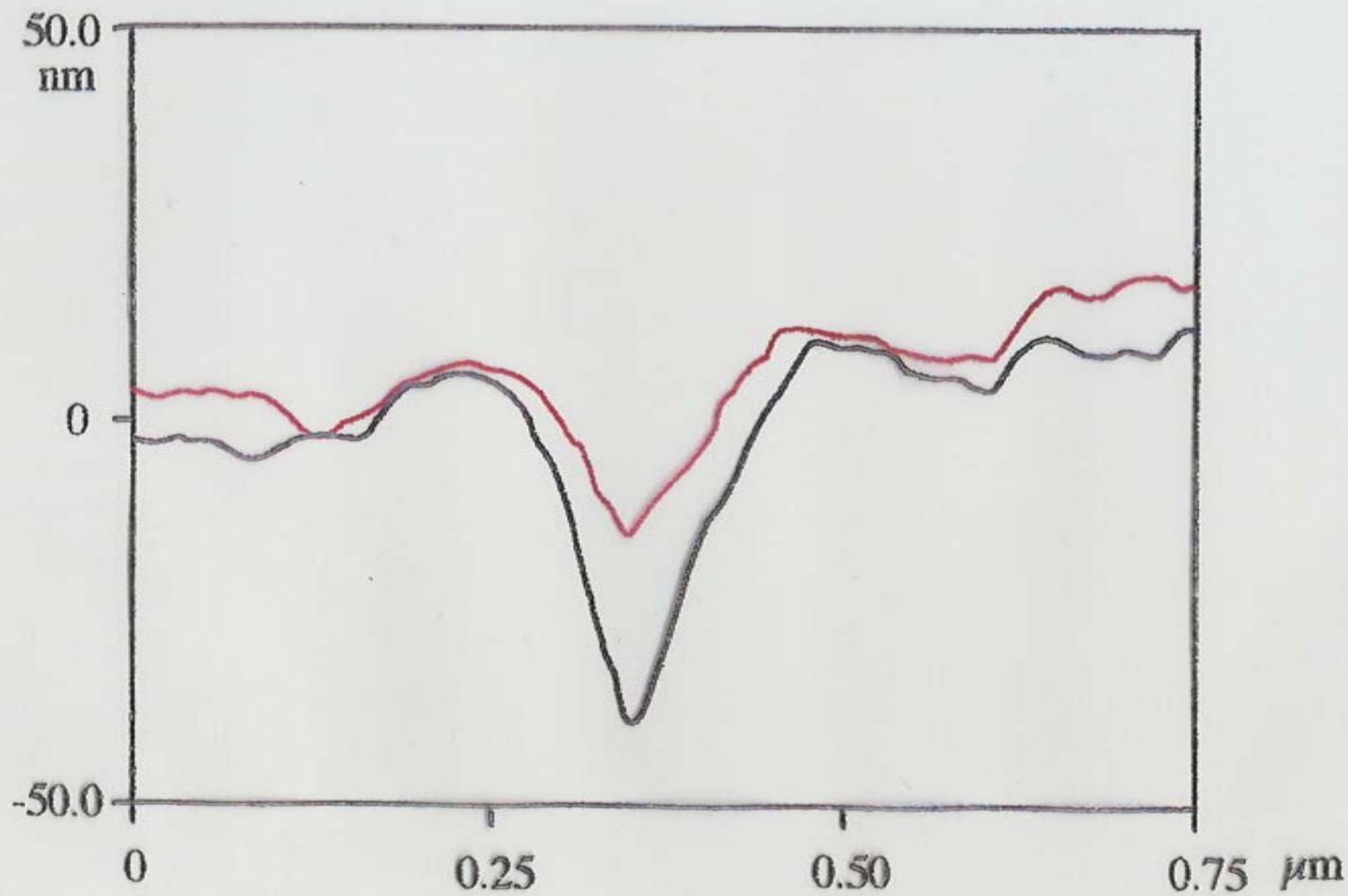


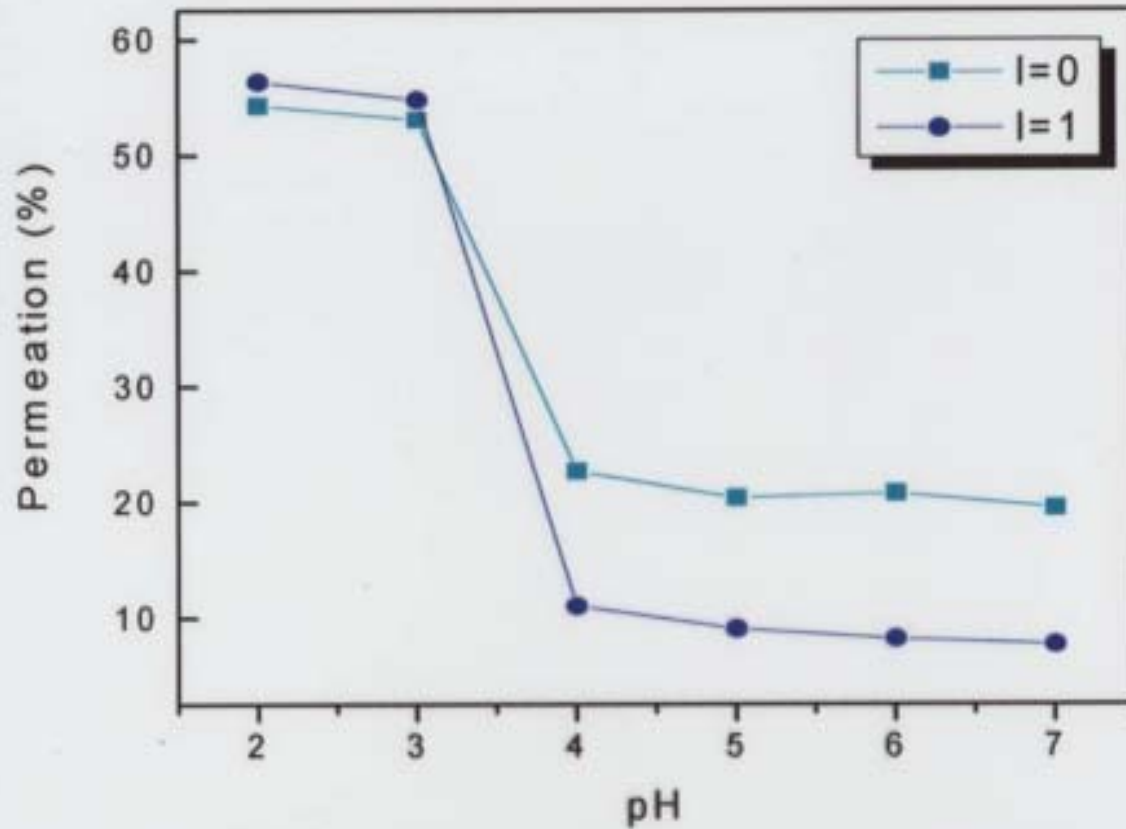
**pH 7.0**



100 nm

(b)



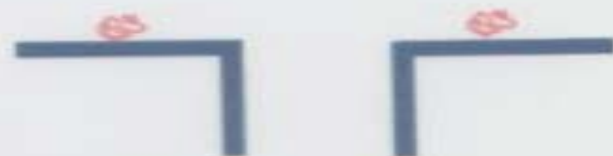


**Relation of permeation, pH and ionic strength for membrane assembled by PAA-HS with graft density of 2 thiols / 100 carboxyls. (3000rpm, 10 min)**

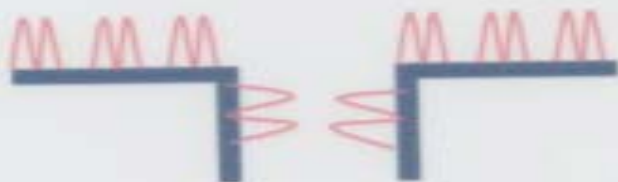
Low



Signal



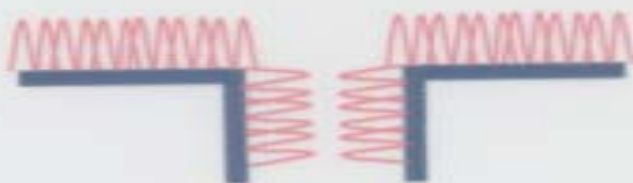
Middle



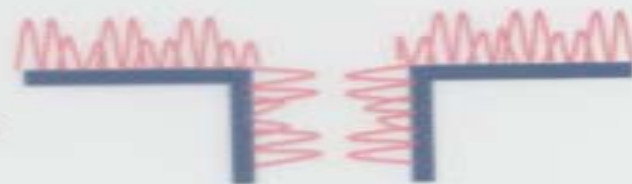
Signal

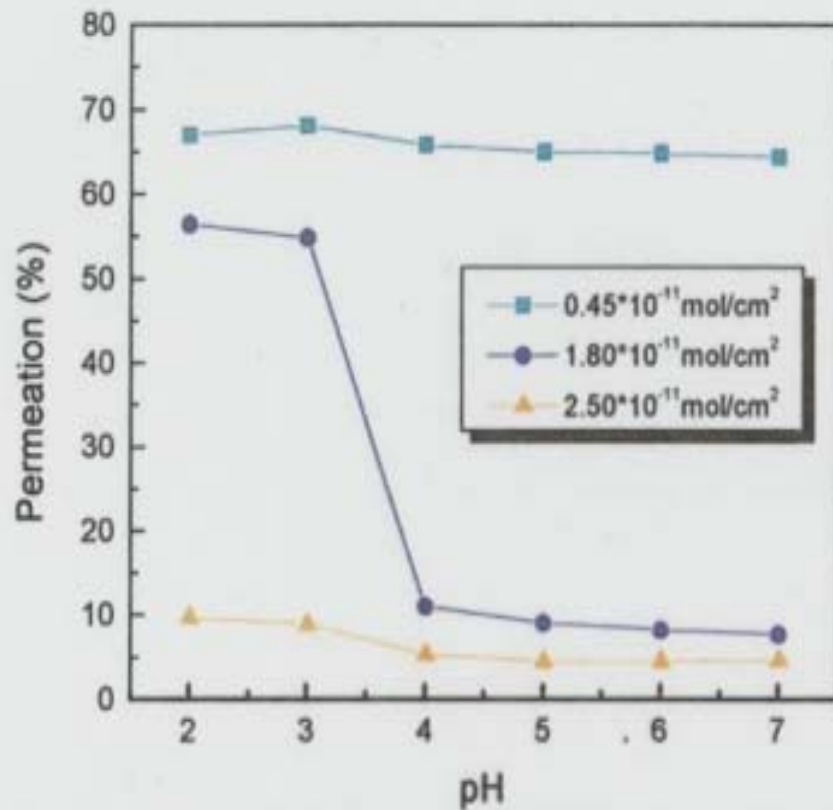


High

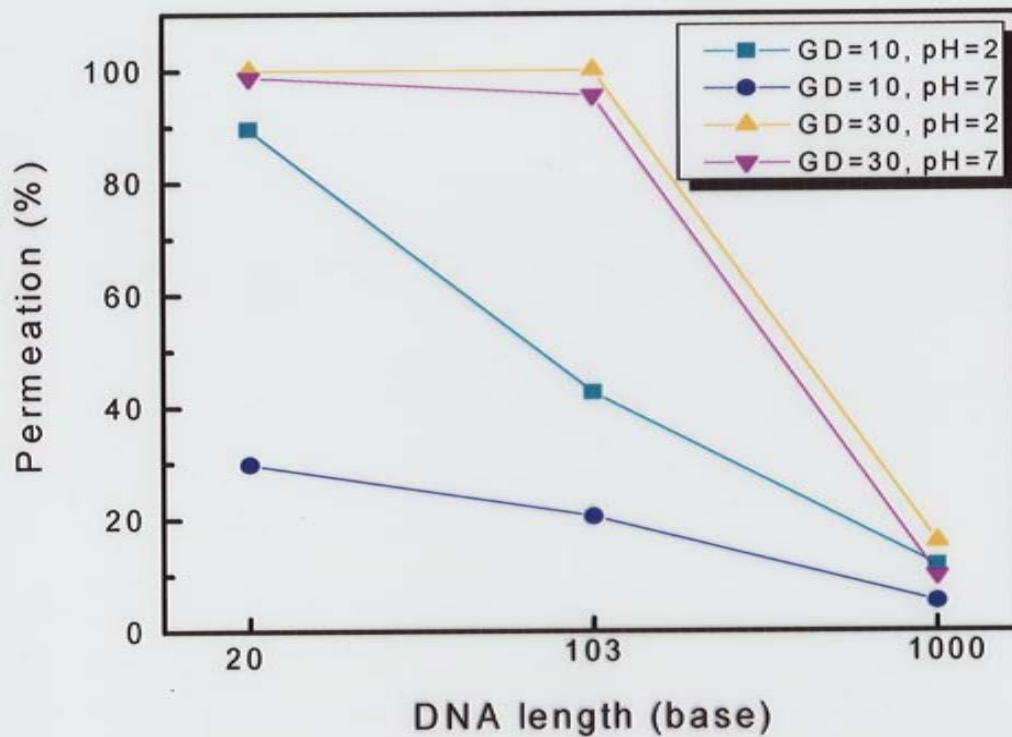


Signal



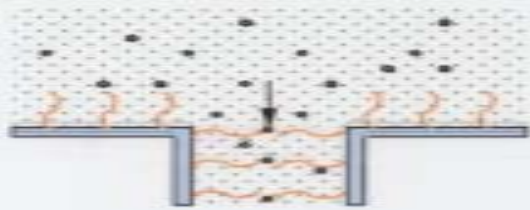


**pH dependence of water permeation for membranes self-assembled by PAA-HS with different surface density (Thiol content: 2 thiols /100 carboxys, 3000rpm, 10 min).**

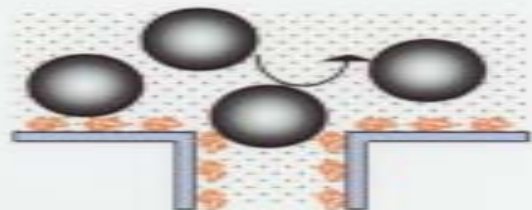
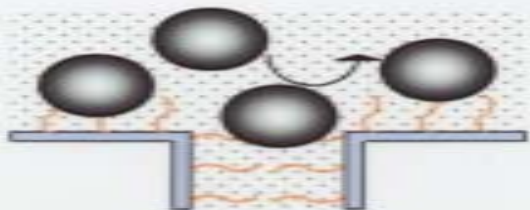
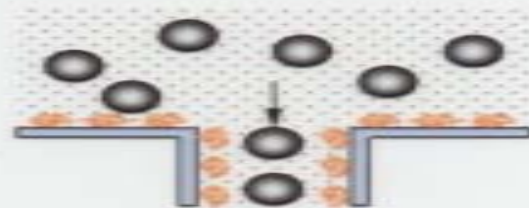
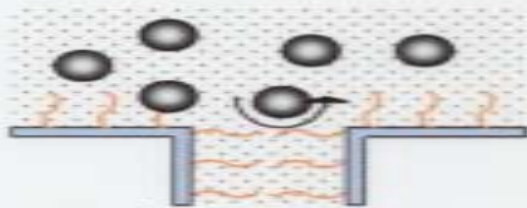
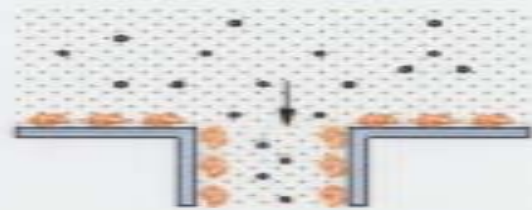


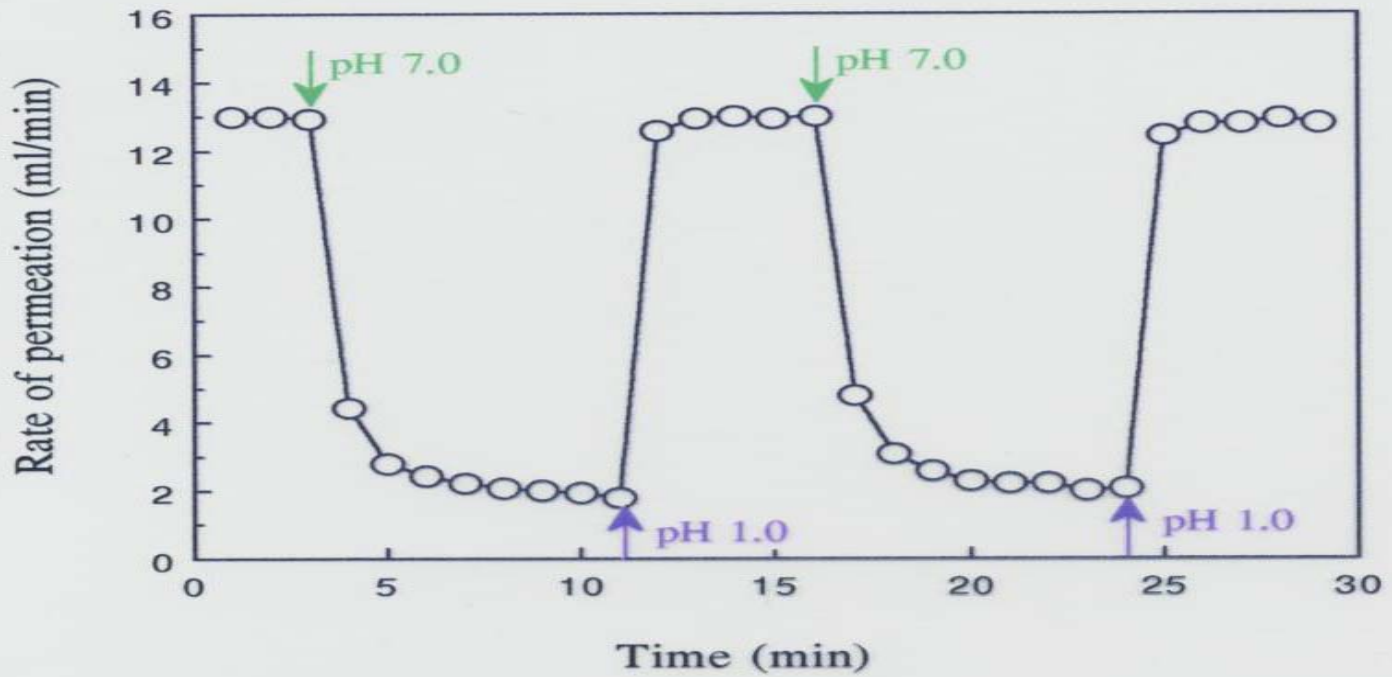
**Relation of DNA permeation, pH and DNA length for membranes assembled by PAA-HS with graft density of 10 and 30 thiols / 100 carboxyls, respectively. (3000rpm. 10 min)**

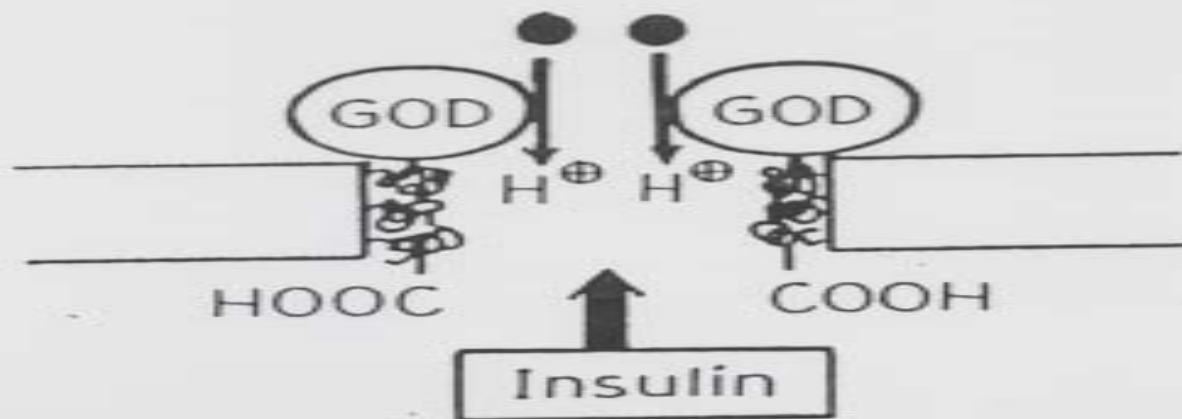
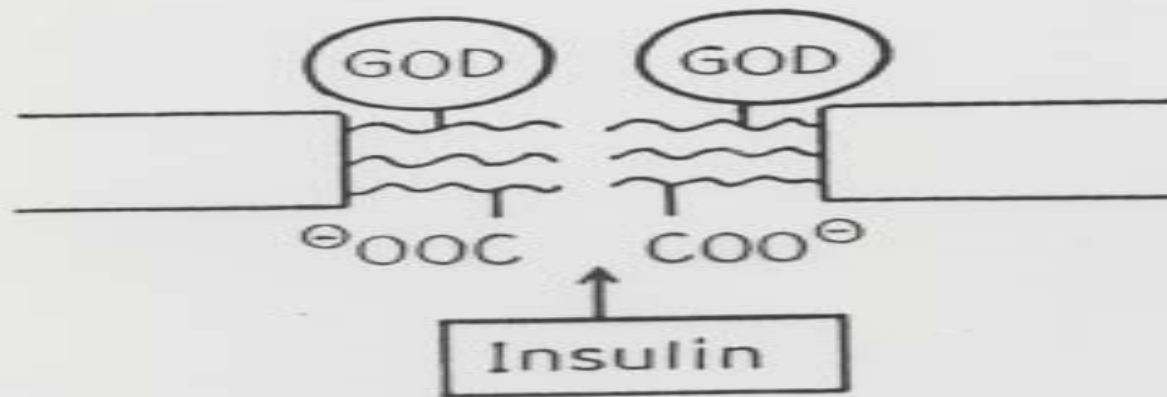
pH=7



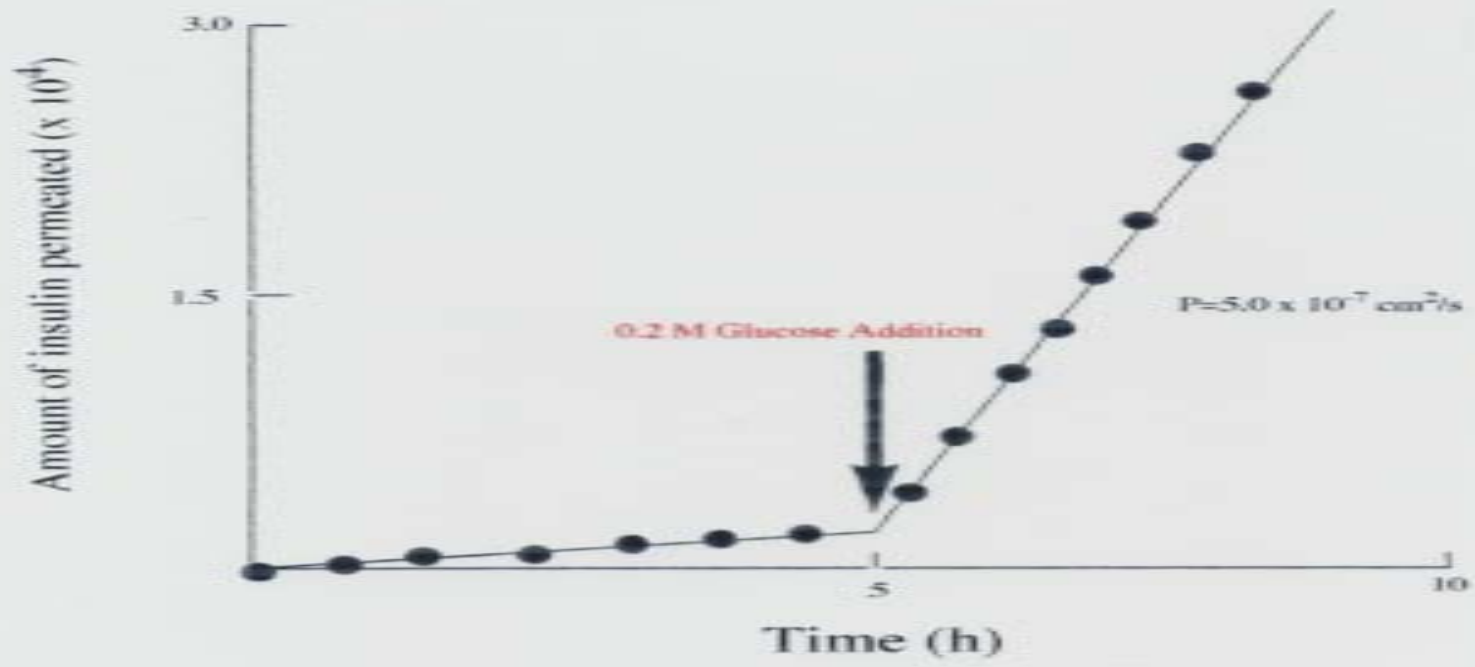
pH=2







● : glucose



# Systems using stimuli-responsive polymers

Regulation of soluble and insoluble states

Regulation of extension of polymer chain

Swelling and shrinkage of polymeric gels



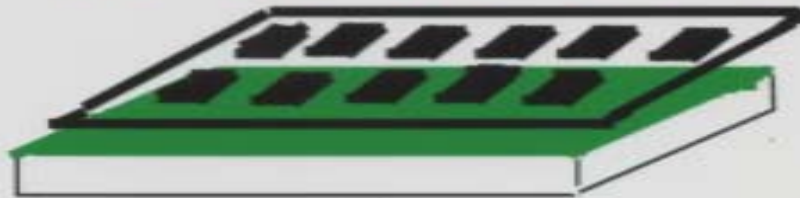
AzPhPAA Coating



Photomasking



UV  
Irradiation

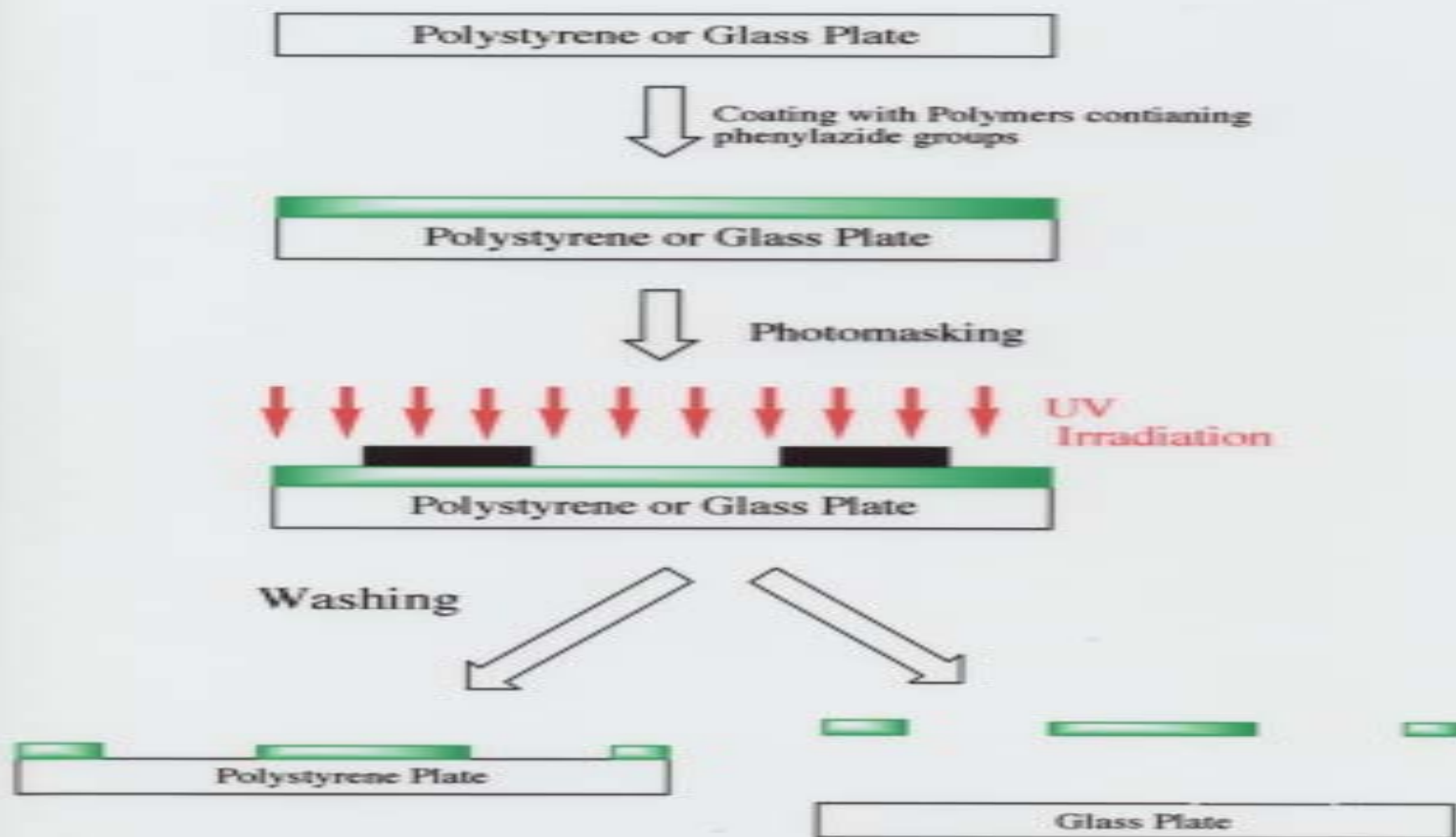


Washing and Removing  
Glass Plate



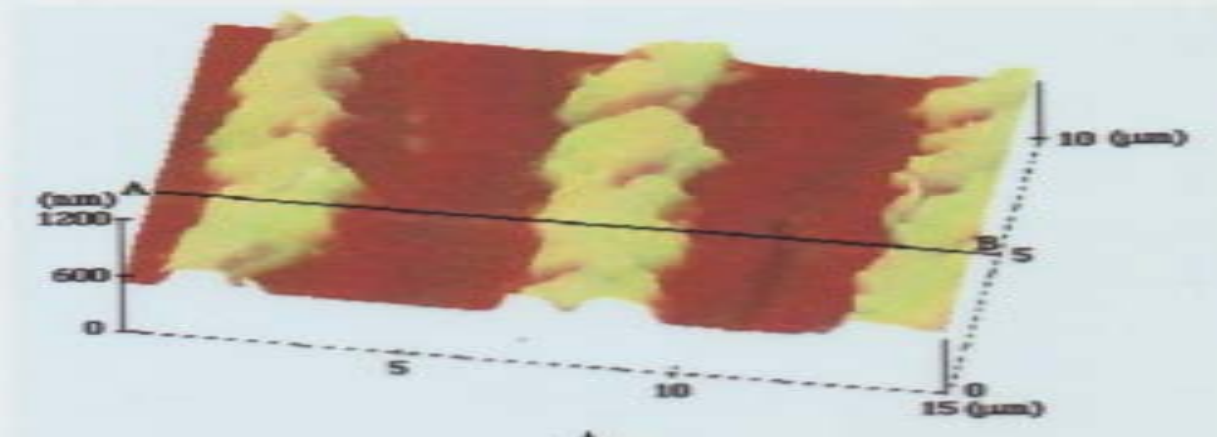


# Microgel Formation on Polystyrene or Glass Plate

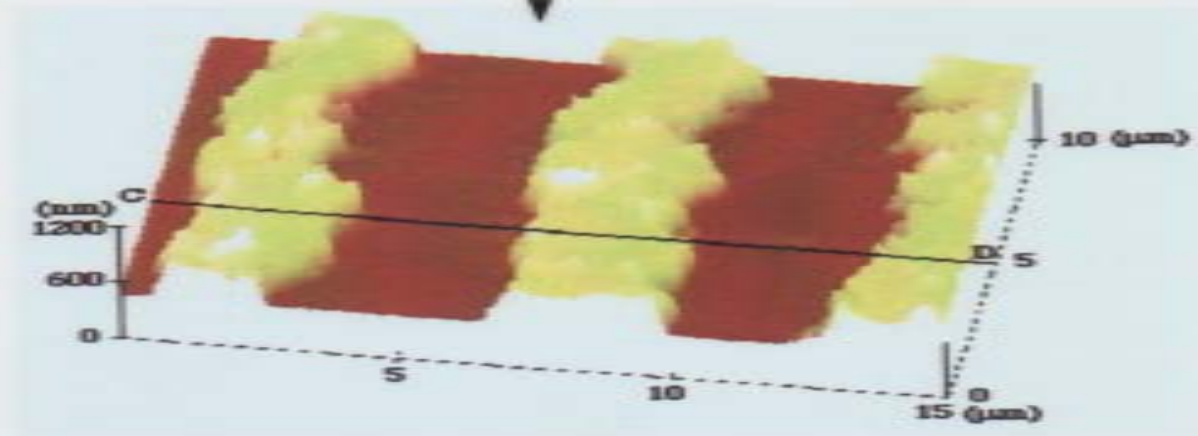


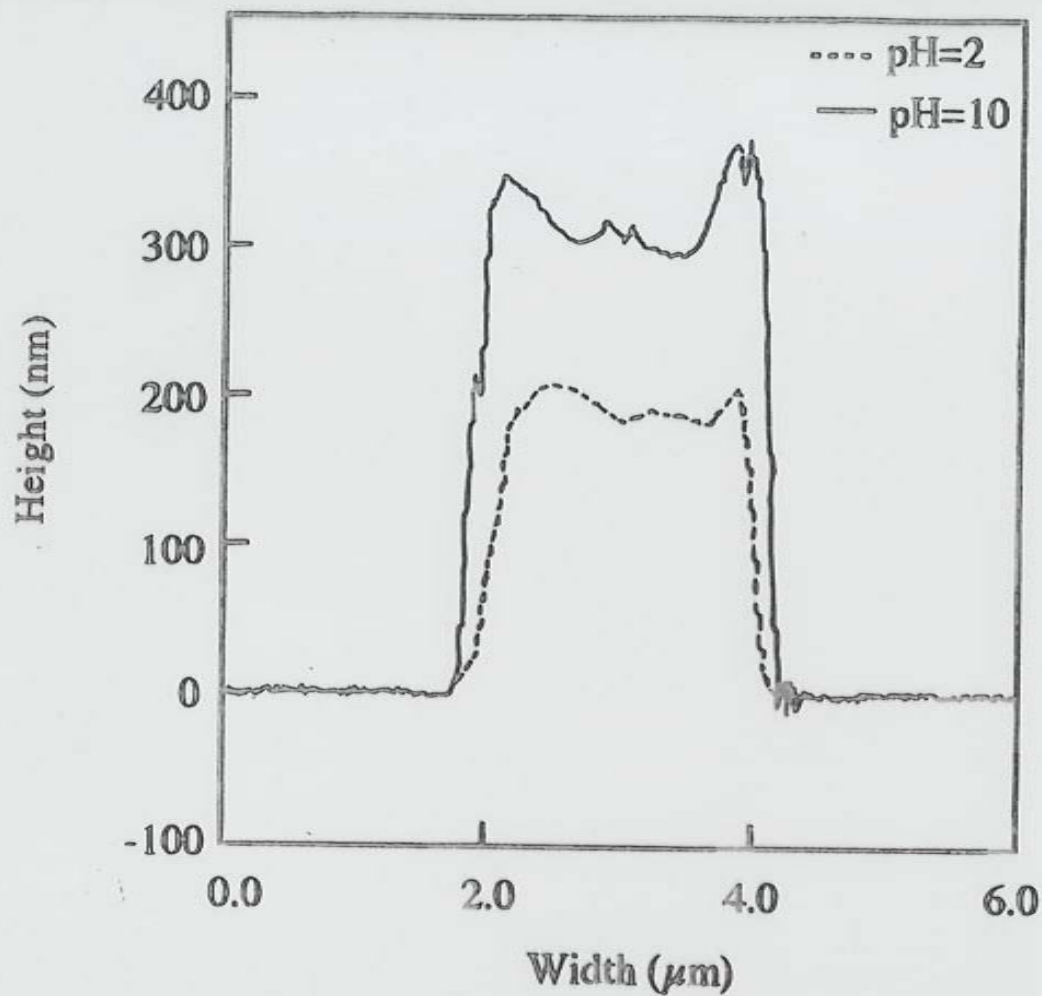
# Atomic force micrograph of pH-sensitive microgel on polystyrene plate

pH 2



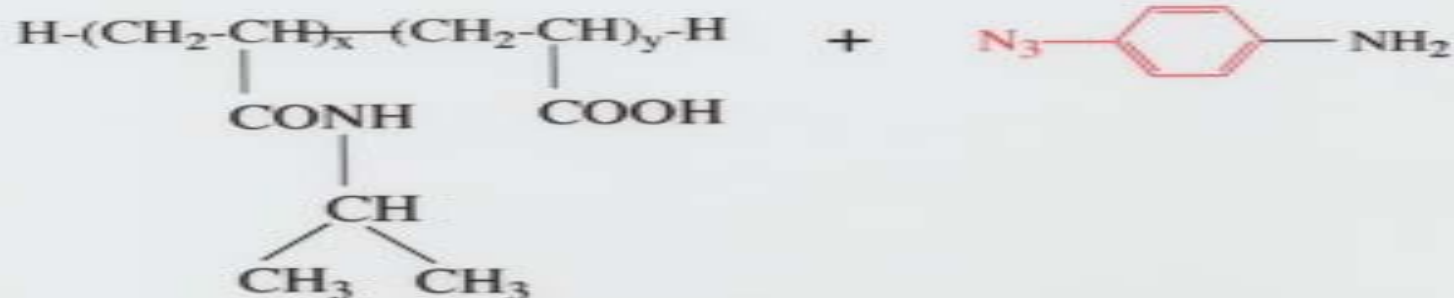
pH 10



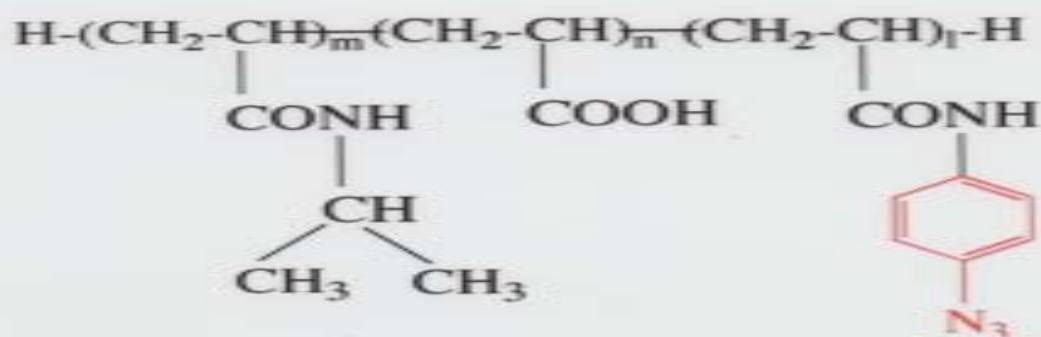


**Figure 3.** Cross-sectional plots of the atomic force micrographs (AFM) of immobilized AzPhPAA microgel network (azidophenyl group content, 14.8%) at pH 2 and 10.

## Synthesis of poly(*N*-isopropylacrylamide-*co*-acrylic acid) carrying azidophenyl groups

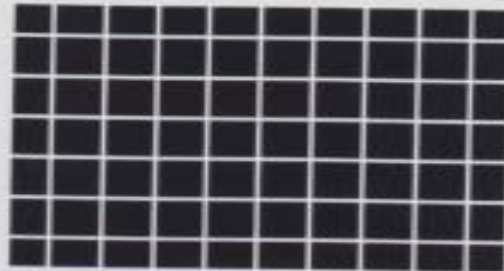


Water soluble carbodiimide  
pH 7.0  
4°C  
48 h



4-azidophenylamidated poly(*N*-isopropylacrylamide-*co*-acrylic acid) (AzPhPIA)

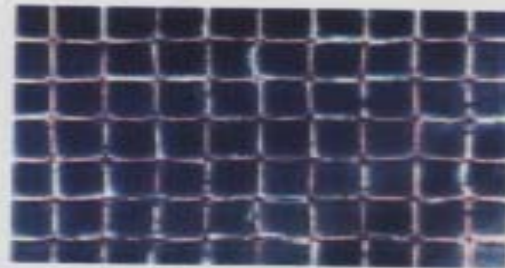
Photomask



— 40  $\mu\text{m}$

Thermo-sensitive microgel prepared on a glass plate and detached from the plate

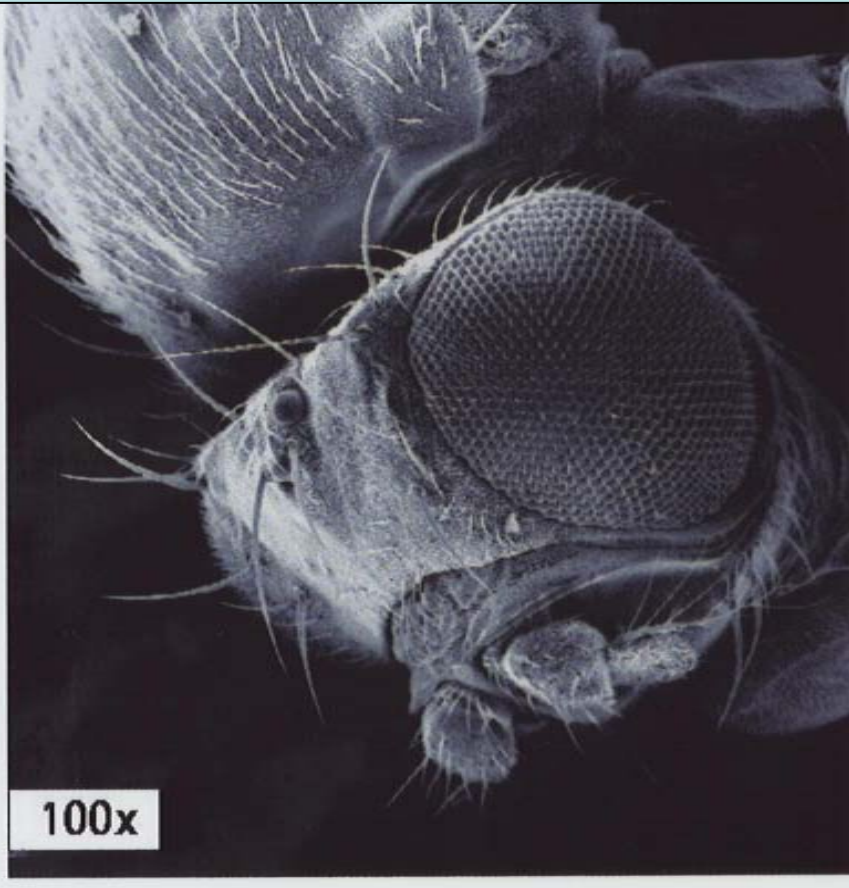
37°C



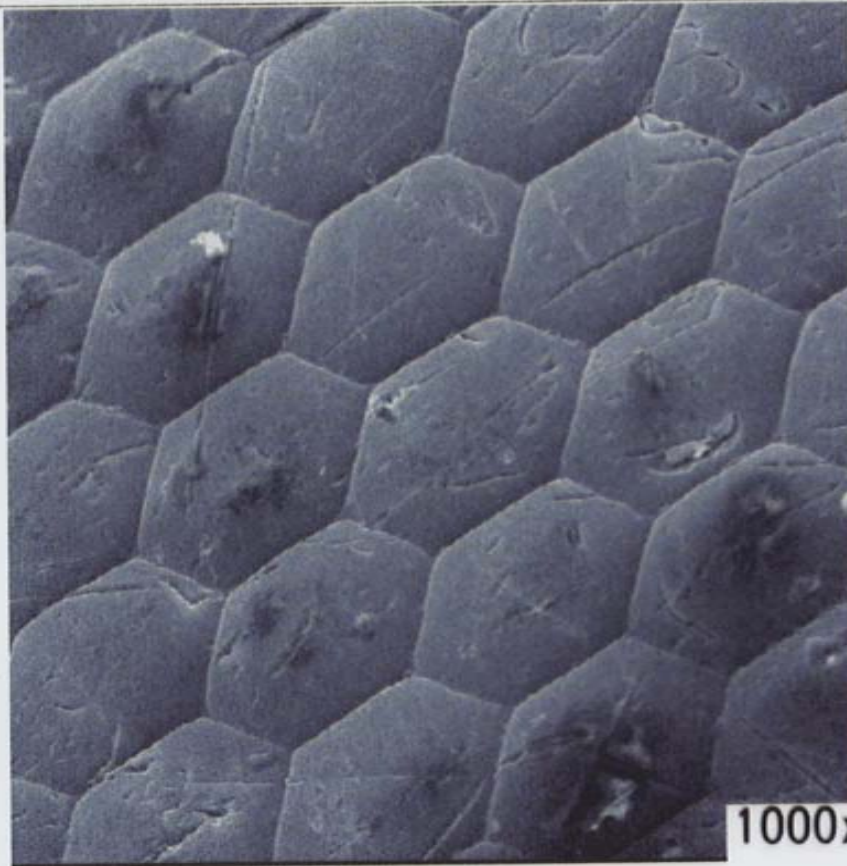
10°C

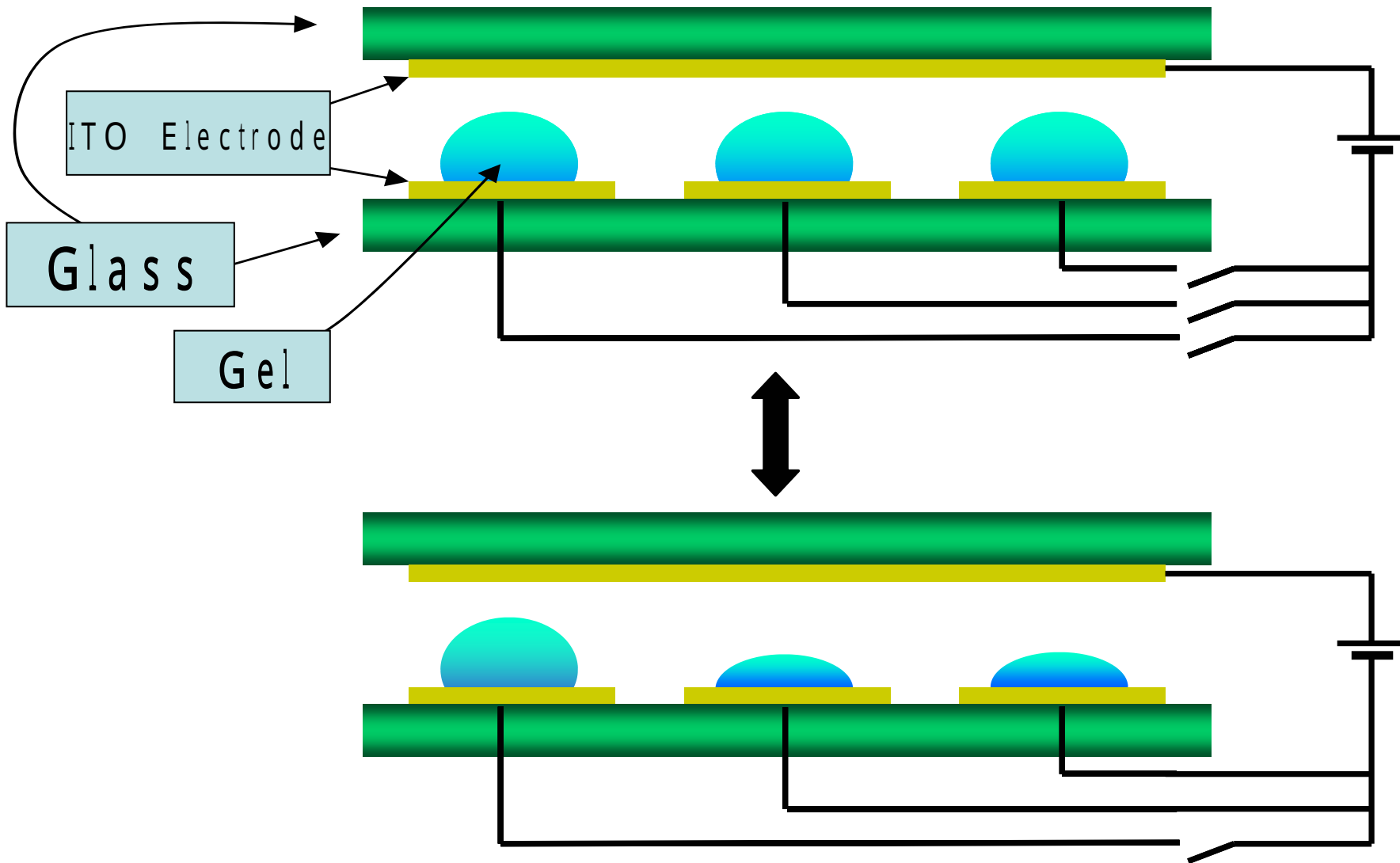


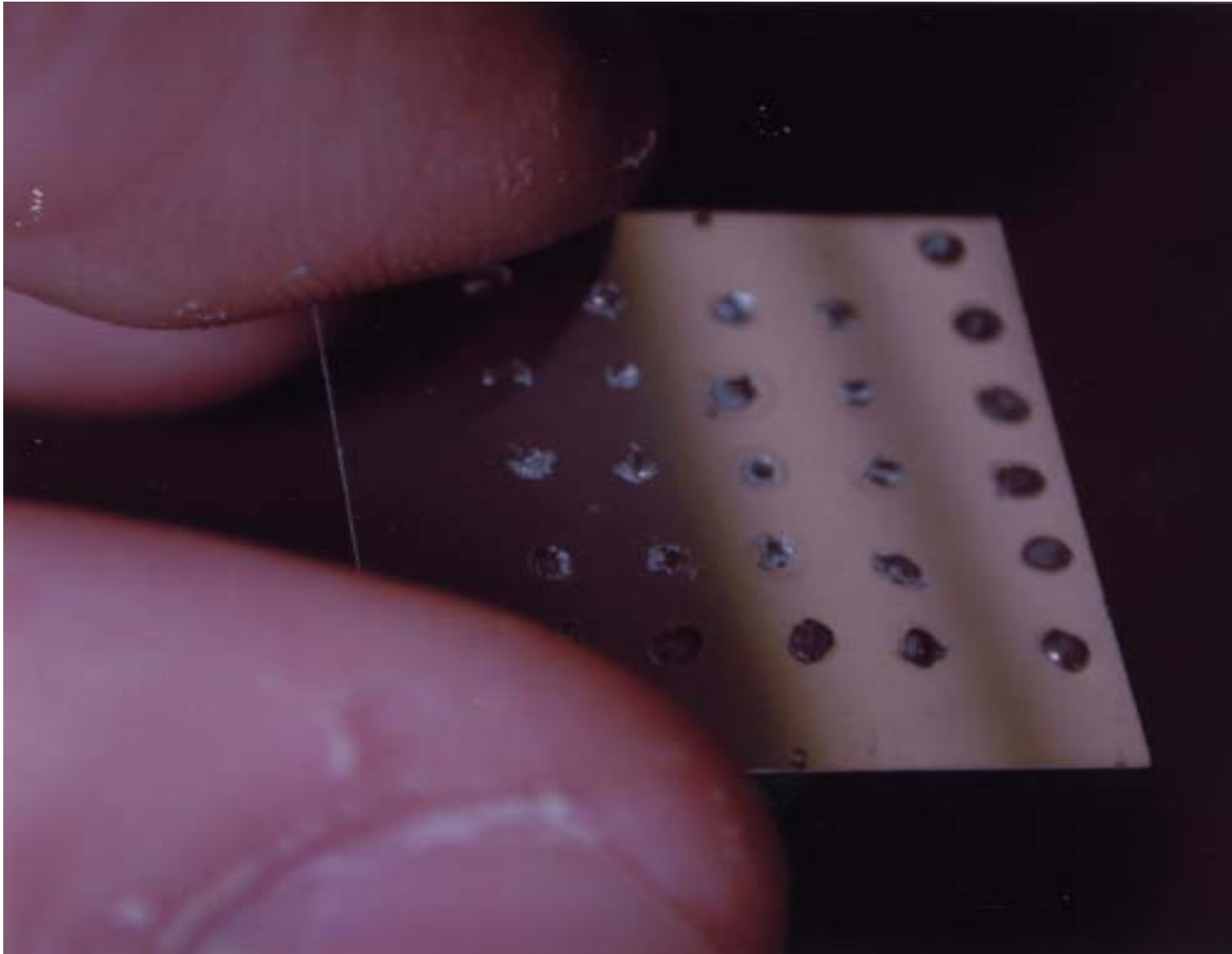
# Compound Eye of Insect

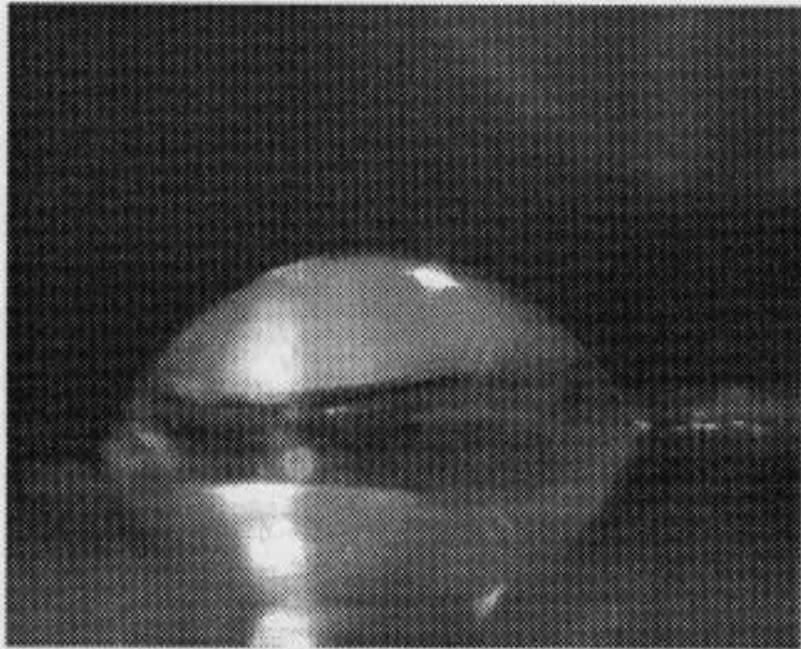


# Compound Eye of Insect

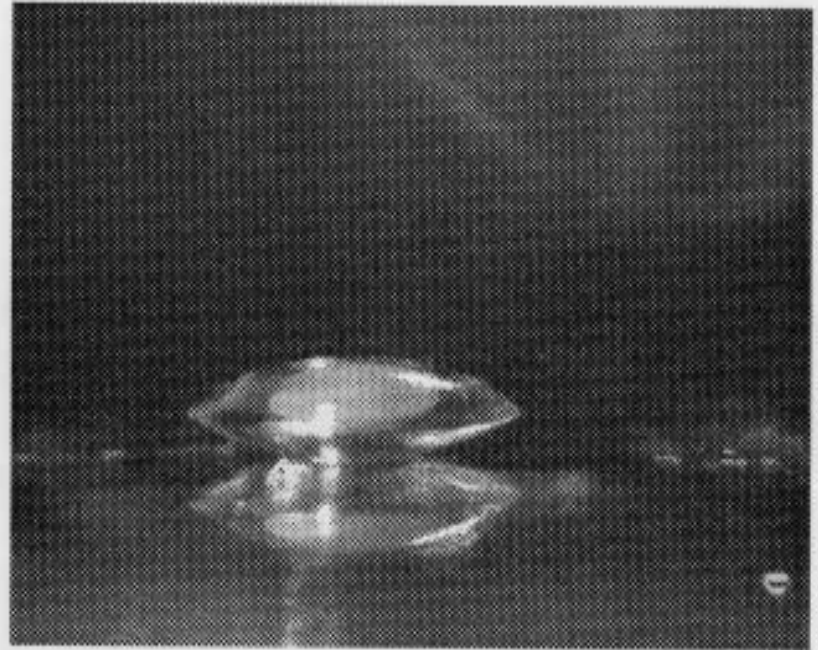








pH7

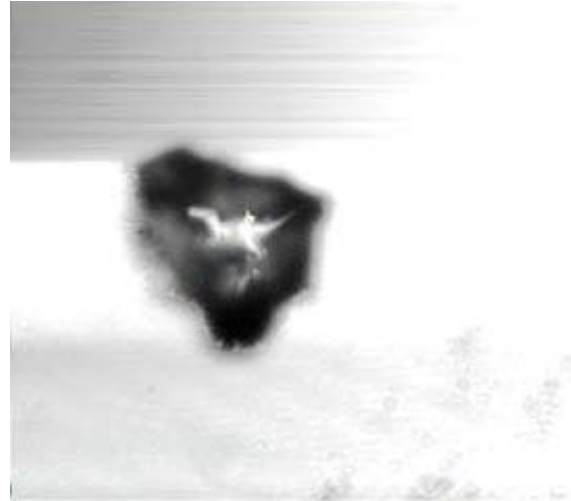


pH3

pH 7



pH 3



Focus length 1100 $\mu$ m

560 $\mu$ m

# Acknowledgements

Regulation of soluble and insoluble states

Dr. O. H. Kwon

Mr. N. Sugimura

Regulation of extension of polymer chain

Dr. Y. S. Park

Dr. H. Zhang

Swelling and shrinkage of polymeric gels

Dr. G. Chen

Dr. J. Ohta