

Stimuli responsive polymers

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Résumé

Cet article est une revue d'un symposium qui s'est tenu durant MACRO 2004 à Paris. C'est un état des lieux sur le comportement de systèmes polymères depuis les simples macromolécules jusqu'aux gels et membranes lorsqu'ils sont soumis à une stimulation physico-chimique. Différents aspects y sont discutés : la synthèse de polymères stimulables, leurs changements de conformation et les applications qui en découlent dans les domaines biomédicaux, membranes, muscles artificiels, actuateurs.

Mots-clés

Polymères stimulables, systèmes hydrophiles et linéaires, gels, membranes.

Abstract

This paper gives the state of the art concerning the behavior of the polymeric systems from single chain in solution to gel and membranes submitted to an external stimuli. It is a report on a symposium held during MACRO 2004 in Paris and it covers different aspects concerning the synthesis or functionalization of stimuli responsive polymers, the changes in conformation, and some applications are discussed like membranes activities, artificial muscles, biomedical possibilities, actuators.

Keywords

Stimuli responsive polymers, hydrophilic linear polymers, gels, membranes.

Changes in conformation and association

Françoise Lafuma (Paris, France) introduced the different recent molecular systems described in the literature involving changes in conformation and/or association depending on external parameters such as pH, solvent composition, temperature, pressure, shear, irradiation, electric or magnetic fields. The richness of effects induced by copolymers depending on composition, molecular weight and architecture was emphasized. The talk was focused on multiresponsive systems. For instance, it has been shown that weakly charged polyelectrolytes of high molecular weight, with a high hydrophobic content, display spectacular reversible shear-thickening properties [1]: in this process a dilute solution of globules becomes an entangled network of coils because intramolecular associations switch to intermolecular associations when shear is applied (*figure 1*). The effect can be coupled with thermal responsiveness by

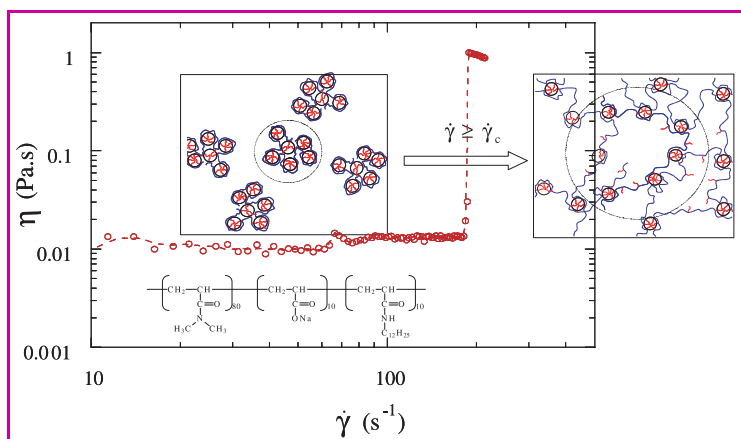


Figure 1 - Typical rheogram for a shear-thickening polymer (molecular weight $2.2 \cdot 10^3 \text{ kg}\cdot\text{mol}^{-1}$ at 1% concentration).

Above the critical shear rate the gelled sample is ejected from the cell.

changing the hydrophobic moieties by thermosensitive ones. For instance when a random copolymer of polyethyleneoxide/polypropyleneoxide ($M_w=2000$) of LCST 30°C is grafted on the structure displayed on *figure 1* instead of the hydrophobic C_{12} units, the system can be triggered together by shear and/or temperature. Similar behaviors can be observed when thermosensitive sequences are incorporated in the main chain [2].

Preparation of new stimuli responsive polymers [3]

The preparation of new stimuli responsive polymers was also discussed by André Laschewsky (Golm, Germany) with emphasis on micellar polymers. After discussing the two major types of switches used hitherto for aqueous media, namely such based on changes of the pH and of temperature, a new switching system was introduced that is based on variations in ionic strength and in ion selective binding, respectively, for zwitterionic polymers. Then, the synthesis of amphiphilic block copolymer, so-called macrosurfactants, was presented. Controlled free radical polymerizations, in particular the RAFT method, were shown to provide a convenient access to such polymers, tolerating the necessary functional groups. Various combinations of switchable amphiphilic structures, containing one or even two switchable blocks, were realized, and their dynamic self-organization in water was discussed. Subsequently, the diblock systems were extended to triblock systems, exemplifying the orthogonal use of complementary stimuli in order to achieve gradual transitions of the systems (*figure 2*).

Functionalization of polymeric membranes [4-6]

Mathias Ulbricht (Essen, Germany) exposed first his recent results on functionalisation of polymeric membranes

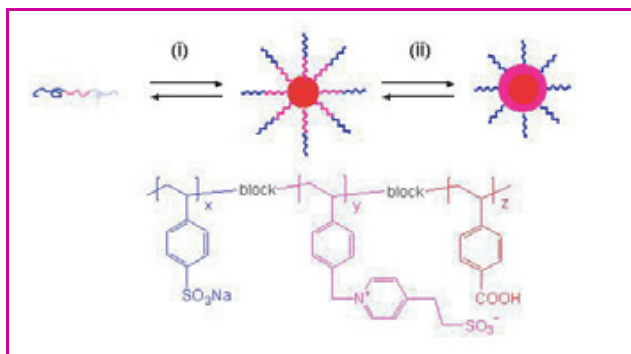


Figure 2 - Example of multiple switching of triblock copolymers in 0.5 aq NaBr.

(i) acidification of the solution induces the collapse of the terminal block (polyvinylbenzoic acid), followed (ii) by dialysis of the brine resulting in the additional collapse of the zwitterionic block. The polymer changes its aggregation state from molecularly dissolved *via* micelles with small cores to micelles with large cores, always providing transparent solutions.

giving specific behaviors in ultrafiltration (as example, he showed the pH dependence of permeability); it is mentioned that membrane switches or valves can be prepared by a controlled grafting of environment-sensitive polymers onto the pore walls of porous polymer membranes. In general, the group follows two different approaches towards advanced functional membranes :

- surface functionalizations of commercial membranes with thin grafted functional polymer layers,
- preparation of polymer composites, either based on compatible functional polymer blends or by pore-filling of polymeric membranes with functional polymers.

From this, M. Ulbricht also introduced the molecular imprinting which yields synthetic receptor sites in polymers which can specifically recognize template molecules. The combination of molecularly imprinted polymers (MIPs) and membranes offers many possibilities for advanced separation processes (*figure 3*). MIP preparation strategies are crosslinking polymerization, e.g. towards thin grafted MIP layers, and/or polymer solidification, e.g. *via* phase separation of polymer blends.

Behaviors of grafted polymeric hydrogels

Kazuyuki Horie (Kobe, Japan) described the mechanism of rapid shrinking of grafted polymer hydrogels studied with scanning microscopic light scattering and fluorescence spectroscopy. Several types of PNIPA gels that shrink much more rapidly than normal NIPA gels by temperature jump were reported. The rapid shrinking of comb-type grafted PNIPA gels may be related to unknown process in kinetics due to the modified structure of network. In order to elucidate the mechanism of the rapid shrinking, the grafted PNIPA gels have been studied by scanning dynamic light scattering (SMLS) and fluorescence spectroscopy (*figure 4*).

Biomedical applications

Allan S. Hoffman (Seattle, USA) showed that conjugation of the smart polymer next to the binding site of a protein, and then thermally-stimulating the polymer to collapse, allows one to block the active site and turns the protein off [7-8]. By reversing the stimulus, one can unblock the site and turns the

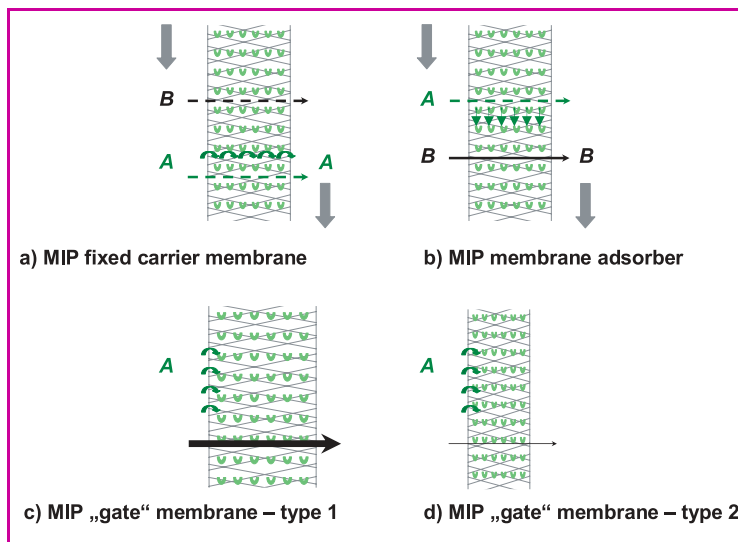


Figure 3 - Separation mechanisms for molecularly imprinted membranes (MIM).

Separation as a consequence of the binding selectivity obtained by imprinting for a substance **A**: **a**) transport of **A** driven by a concentration gradient is facilitated *via* binding/desorption to neighbored MIP sites, while the non-specific transport of another substance **B** by diffusion is hindered by the micropore structure of the membrane; **b**) transport of **A** is retarded either by binding or binding/desorption to MIP sites on the surface of trans-membrane pores, while another substance **B** which has no specific interactions with the membrane surface will be transported by diffusion or convection; **c**) MIM permeability is increased, e.g. due to an increase of membrane (barrier) swelling as a consequence of **A** binding to MIP sites; **d**) MIM permeability is decreased, e.g. due to a decrease of membrane (barrier) swelling as a consequence of **A** binding to MIP sites.

protein back on. In a different approach, Hoffman reported on the grafting of both PNIPAAm and PEG-biotin on aminated latex nanoparticles, to yield a new chromatographic matrix. The beads may be thermally-stimulated to aggregate *via* PNIPAAm-driven aggregation. This nanobead aggregation phenomenon has been utilized in microfluidic devices, where the beads adhere to the walls of the microfluidic channels. Streptavidin was bound to the biotin-PEG that was attached to the bead surfaces, and then biotinylated antibodies, ssDNA or enzymes have been bound to the streptavidin. This has functionalized the bead matrices for conducting

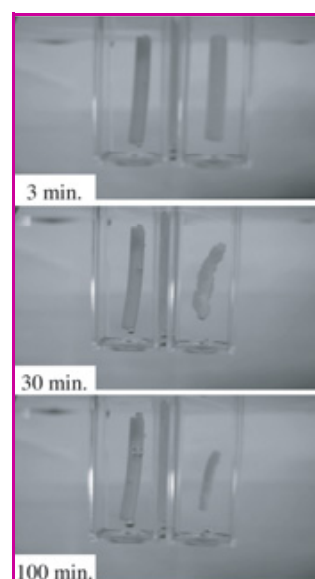


Figure 4 - The shrinking of gels induced by temperature jump (25°C → 40°C).

The left is the normal gel and the right is the grafted gel.

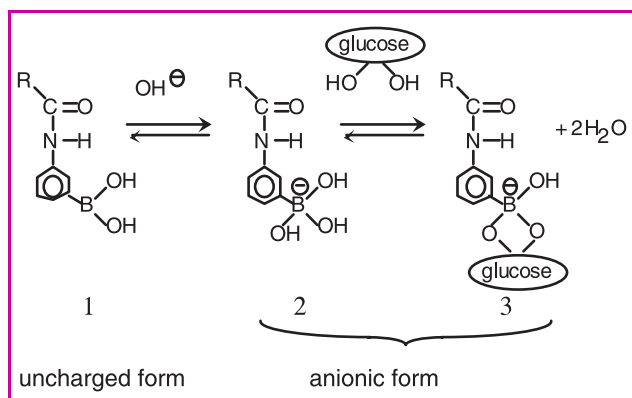


Figure 5 - Equilibria of (alkylamido)phenylboronic acid in an aqueous solution in the presence of glucose.

immunoassays, affinity separations and enzyme bioprocesses within a microfluidic device format. This system is currently being developed by Hoffman and his colleague, Patrick S. Stayton, as microfluidic devices for point-of-care diagnostics, affinity separations and bioprocesses.

Kazunori Kataoka (Tokyo, Japan) demonstrated that he can prepare gels grafted with specific groups to recognize glucose (phenylborate moiety) and responsive to glucose concentration (controlled by the swelling degree) for use as a self-regulated insuline delivery system for the treatment of diabetes at physiological conditions (37 °C, pH = 7.4) [9-11]. A basis of the system is the shift in the equilibrium between the uncharged and charged form of phenylboronic acid moieties in the polymer chain thorough complex formation with glucose as shown in *figure 5*. An increased glucose-concentration shifts the equilibrium in the direction of increasing fraction of borate anions (**2 + 3**) and decreasing the fraction of the uncharged form (**1**). Thus, an amphiphic gel composed of such as Nisopropylacrylamide (NIPAAm) bearing a proper amount of phenylborate moiety undergoes a sharp volume phase transition in response to change in the glucose concentration under isothermal condition, due to a change in the gel hydrophilicity as well as a concomitant change in ion osmotic pressure. The on-off regulation of insulin release from the gel in response to change in glucose concentration was also demonstrated.

Artificial muscles

Yoshihito Osada (Sapporo, Japan) proposed to use polymer gels to create biomimetic mobility systems (*figure 6*), focusing to their reversible size and shape change, thereby realizing motion by integrating the deformation on a molecular level [12-15]. With his group, he prepared a synthetic system based on natural species: bio-nanomachines built of actin and myosin fiber gels, which are able to move faster than native actin fiber, were presented (*figure 7*). The mechanism of the motion associated with hierarchical structure was discussed. Chemically cross-linked actin gel filaments, several thousand times the volume of native actin filaments (F-actin), move along a chemically cross-linked myosin fibrous gel with higher velocity than that of native F-actin in 3 sec, by coupling to ATP hydrolysis. This kind of protein gel machine of the desired shape, size and function might be used in artificial limbs or artificial organs. In addition the immune system of body might accept implants made from human muscle.

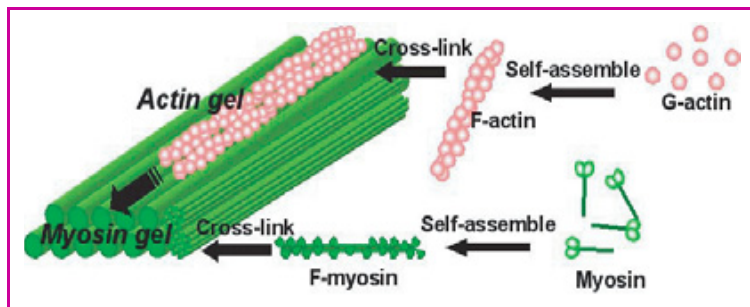


Figure 6 - Schematic illustration of gel machine built from muscle proteins by self-organization and chemical cross-linking.

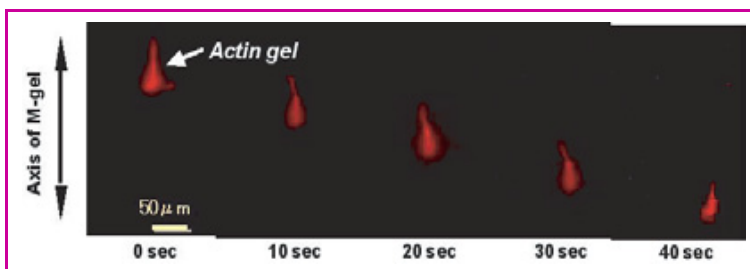


Figure 7 - Sequential fluorescent images of the movement of actin gel on the oriented myosin gel.

Actuators

Claude Chevrot (Paris, France) presented new actuators based on conducting interpenetrating polymers networks [16-18]. As described on *figure 8*, the basic concept of an actuator which can be operated in open air is to apply a voltage between two electrodes bearing an electroactive material and separated by a thin layer of an ionic conductor preferentially in the solid state (usually a solid polymer electrolyte, SPE). As a consequence, the life time of such three-layer based actuators is limited by the delamination process due to a poor adhesion between the layers. The polymerization of EDOT inside a network or an IPN based on polyethyleneoxide (PEO) and polybutadiene networks has attracted attention because these molecular architectures exhibit numerous advantages over blends. Moreover, PEDOT exhibits a good conductivity for various applications, i.e. electrochromic and actuator devices, and also is one of the most stable CP in air notably in the oxidized state. By chemical polymerization of EDOT inside IPN matrix having different PEO/PB ratio, "one-piece" system is obtained

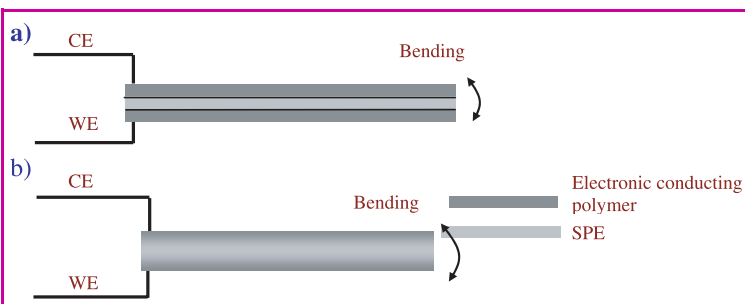


Figure 8 - (a) Three-layer actuator. The solid polymer electrolyte is sandwiched between two electronic conducting polymers acting as electrodes. (b) "Gradient" one piece system actuator where the electronic conducting polymer is selectively embedded towards the outside faces of the SPE IPN matrix.

which is similar to a layered one with the advantages the intimate combination of polymers needs no adhesive interface avoiding delamination (*figure 8b*). The association of PEDOT and PEO into IPN will be favored by the presence of ethylene oxide groups in both components which should improve their compatibility. As in many actuators based on conducting polymers, the choice of the solid polymer electrolyte system is critical in order to be operating efficiently in open air. Aqueous solution or organic solvent containing electrolytes have been used widely although drying process could never be prevented. Recently Chevrot *et al.* used a room temperature ionic liquid as electrolyte leading to perform more than 10^6 cycles without neither delamination nor degradation of the conducting polymer. This material is capable to work in open air over a period of six months and shows 90° angular deflexion under an applied voltage of ± 5 V with frequencies from 1 to 18 Hz.

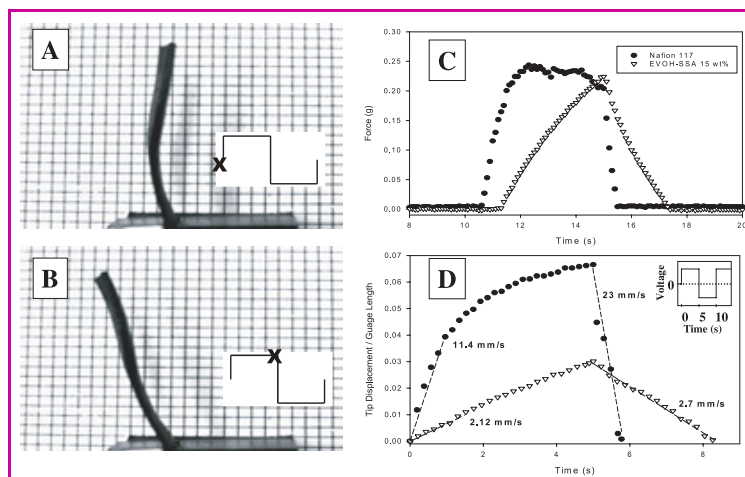


Figure 9 - Images A and B show the deflection of a 15 wt% SSA modified EVOH IPMC actuating under an 8 V, 0.1 Hz square wave signal.

Image A shows the initial position (0 sec) and image B the position at 5 sec after excitation. Image C shows the load cell response of Nafion® 117 and 15 wt% EVOH-SSA IPMC's. Image D shows the tip displacement profiles of the same IPMC's with an overlay showing the excitation wave.

Electric and magnetic field responsive materials

A novel class of sulfonated ethylene vinyl alcohol copolymers has been synthesized by Robert B. Moore (Hattiesburg, USA) and artificial muscles produced from this class of materials [19]. FT-IR spectroscopy confirmed the formation of the crosslinked and sulfonated membranes and the effect of crosslinking on crystallinity. Small angle X-ray scattering and solid-state ^{23}Na NMR verified the existence of both ionic aggregates and an electrostatic network within the matrix. In comparison to the standard IPMC material Nafion®, the EVOH ionomer has a less defined electrostatic network including a large population lone ion pairs dispersed through the matrix. Pulsed gradient NMR techniques revealed the diffusion of water through modified EVOH was three times slower than Nafion®, attributed to the less defined ionic network. Ionic polymer metal composites were produced through an electrodeless deposition of platinum generating membranes that display actuation under applied electrical stimulus (*figure 9*). Video analysis and actuation force measurements showed the modified EVOH IPMC's behave similar to Nafion®, yet the kinetics of actuation are significantly slower. As shown in *figure 9C*, the Nafion® IPMC builds force rapidly and relaxes with time. In contrast, the EVOH-SSA based IPMC shows a nearly linear increase in force through the excitation cycle. Similar behaviors are shown in the tip displacement profiles of *figure 9D* in addition to the disparity in tip velocity with Nafion® IPMC's moving five times faster than modified EVOH. The disparity in actuation kinetics has been attributed to slower water diffusion through the EVOH matrix.

The new generation of magnetic filed responsive gels and elastomers proposed by Miklós Zrinyi (Budapest, Hungary) represents a new type of composites, consisting of small (mainly nano-sized) magnetic particles dispersed in a high elastic polymeric matrix [20-21]. The particles couple the shape of the elastomer to the external magnetic fields. Shape distortion occurs instantaneously and disappears abruptly when external fields are applied or removed, respectively. Combination of magnetic and elastic properties leads to a number of striking phenomena that are exhibited in response to impressed magnetic fields. Giant deformational effect, tuneable elastic modulus, non-homogeneous deformation and quick response to magnetic field open new opportunities for using such materials for various applications (*figure 10*). In uniform field there are no attractive or repulsive field-particle interactions therefore particle-particle interactions become dominant. In monomer solutions, containing dispersed magnetic particles, the imposed field orients the magnetic dipoles. Due to the attractive forces pearl chain structure develops. The ordered structure can be fixed by cross-linking polymerisation. The anisotropy manifests itself in both direction dependent elastic modulus as well as direction dependent swelling. The magnetic field responsive gels have shown a change in compressive modulus under uniform magnetic field. Depending on the orientation of particle chains in the network and that of the magnetic field, the induced temporary reinforcement may exceed one order of magnitude. These results suggest that magnetic field responsive gels and elastomers have several potential applications as tuned vibration absorbers, stiffness tunable



Figure 10 - Snapshot of shape change of a magnetite loaded polyvinyl alcohol hydrogel due to modulated magnetic field. The frequency of the field is 40 Hz.

mounts and suspensions. Since the magnetic fields are convenient stimuli from the point of signal control, therefore it is of great importance to develop and study such soft and flexible magnetic systems.

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