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# Semi-interpenetrating Polymer Networks of Polyelectrolytes

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## Abstract

This review is devoted to synthetic pathways, swelling-deswelling behavior, physico-chemical and physico-mechanical properties as well as stimuli-sensitivity of semi-interpenetrating polymer networks (SIPNs) based on crosslinked and linear polymers. The main attention is paid to systems composed of neutral or charged three-dimensional networks with embedded neutral or charged macromolecules. The peculiarities of template (*co*)polymerization of hydrophilic monomers in the presence of water-soluble polymers as a matrix are emphasized. Nonionic hydrogel matrixes, namely polyacrylamide, poly(acrylamide-*co*-acrylic acid), poly(*N*-isopropylacrylamide) that are able to exhibit the sensitivity to dielectric permittivity, pH and temperature are mostly considered. Typical water-soluble polymers which serve as a matrix and are immobilized within networks represent the sensitive to environment water-soluble nonionic, anionic, cationic and amphoteric ones. Some examples of alginate and chitosan based SIPNs are demonstrated because these polysaccharides distinguish by commercial availability and biodegradability. Synthetic protocols of the organic-inorganic hybrid SIPN as well as hydrogel-protein SIPN are given. The SIPNs obtained by interpolyelectrolyte reactions, *e.g.* by interaction of ionic networks with oppositely charged linear macromolecules at gel-solution interface are also exemplified. The SIPNs containing enzymes, catalytic active functional groups, polymer-metal complexes, and nanoparticles exhibit high catalytic activity in hydrolysis, hydrogenation and decomposition of low-molecular-weight substrates. Structural, morphological, physico-chemical and physico-mechanical properties of SIPNs are determined by both network structure and nature of immobilized linear polymers. Application aspects of SIPN include drug delivery systems, pervaporation and fuel cell membranes, gel-immobilized nanosized catalysts, solar technology *etc*.

## Introduction

Hydrogels are three-dimensional polymer networks that swell significantly and/or exhibit significant changes in response to environmental signals, such as temperature, pH, ionic strength, electric field, and magnetic field, called stimuli-sensitive hydrogels [1,2]. There are many different stimuli to modulate the response of polymer systems. These stimuli could be classified as either physical or chemical stimuli [3]. Chemical stimuli, such as pH, ionic strength and chemical agents, will change the interactions between polymer chains or between polymer chains and solvents at the molecular level. The physical stimuli, such as temperature, electric or magnetic fields, and mechanical stress, will affect the level of various energy sources and alter molecular interactions at critical onset points. These responses of polymer systems are very useful in bio-related applications such as drug delivery [4], biotechnology [5], and chromatography [6,7]. Some systems have been developed to combine two or more stimuli-responsive mechanisms into one polymer system [8]. For instance, temperature-sensitive polymers may also respond to pH changes. On the other hand, two or more signals could be simultaneously applied in order to induce response in so-called dual responsive polymer systems. Among the numerous temperature- and pH-sensitive hydrogels the most investigated are poly(*N*-isopropylacrylamide) (PNIPAAm), which exhibits a distinct phase transition at a lower critical solution temperature (LCST) between 30 and 35°C,

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and poly(acrylic acid) (PAAc) and its sodium salt-poly(sodium acrylate), which swell at pH values above the $pK_a$ of PAAc (4.75) and shrink at pH values below the $pK_a$ of PAAc.

Dual temperature- and pH-responsive behavior can be simply achieved by incorporating NIPAAm and acrylic acid (AAc) as random comonomers by copolymerization. Another approach involves the formation of interpenetrating or semi-interpenetrating networks from these monomers [9-11]. The individual properties of the two components in the networks depend not only on their phase separation morphologies, such as size and shape of the phases, but also on the interactions between the two systems. Greater phase separations, that is, larger phase domains and sharp interfaces, show the characteristics of the individual components, whereas more compatible and smaller phase domains give less distinct individual behaviors.

Synthesis and characterization of SIPNs are of great interest due to improvement in the flexibility and mechanical properties of hydrogel materials [12-14], biomaterials [10] and design of stimuli-sensitive compositions [15-17]. Interpenetrating polymeric networks (IPNs) are three-dimensional structures which represent double network gel (Fig. 1a). Commonly accepted methods used for preparation of IPNs are sequential and simultaneous network formation. In the former case the first polymer network is formed then the second monomer, crosslinker and initiator are polymerized *in situ*. In the latter case the mixture of at least two monomers, crosslinking agent and initiator are mixed followed by simultaneous polymerization.

According to IUPAC nomenclature the SIPNs are distinguished from the IPNs because the constituent linear or branched polymers can, in principle, be separated from the constituent polymer network(s) without breaking chemical bonds; they are polymer blends. The structural model of SIPNs can be represented as a spatial network with physically entrapped linear macromolecules (Fig. 1b). SIPNs are defined as solutions that include two independent components, where one component is a crosslinked polymer and the other component is a non-crosslinked polymer. The crosslinked polymer preferably constitutes between about 10 and 90% by weight of the semi-interpenetrating network composition. The SIPNs are preferably prepared from hydrophilic polymers. In one embodiment, the polymer networks include a hydrophilic polymer with the groups crosslinkable with active species and/or ionically crosslinkable groups, and a hydrophilic polymer with no active species or ionically crosslinkable groups.

Even though the stimuli responsive polymers are attractive for their potentials, they have to overcome several barriers; rapid response, mechanical strength, reproducibility, biocompatibility, biodegradability, nontoxicity and so on, according to their applications. Many trials to fulfill these requirements have been reported in recent years. Therefore we expect that our systematic review of SIPN trials could help chemists as well as non-chemists to develop new stimuli responsive polymers or polymeric systems which could be reliably utilized in real life applications.

## Synthesis and Characterization of SIPNs

The SIPNs may be divided into several types. *Type 1* represents hydrophilic network with immobilized linear polyelectrolytes having nonionic, anionic, cationic or amphoteric character. *Type 2* is charged networks with embedded nonionic (or neutral) linear polymers. *Type 3* is hydrogel–hydrogel composite consisting of macroporous gel matrix with dispersed

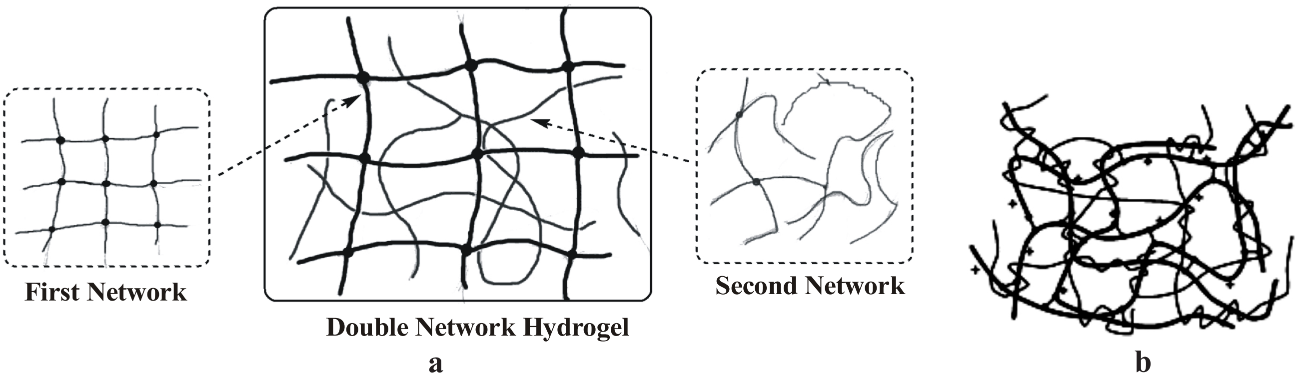

Fig. 1. Schematic representation of IPNs (a) and SIPNs (b).

micro- or nanogels. *Type 4* is a product of interaction between the oppositely charged networks and linear polyelectrolytes. In some cases inorganic gels, such as $(SiO_2)_n$ or $(TiO_2)_n$, can also serve as three-dimensional network matrix.

Template (co)polymerization is widely used for synthesis of SIPNs [18]. In this case ionic monomers are pre-adsorbed by template through electrostatic interaction while neutral monomers are randomly distributed in reaction medium without interaction with template (Fig. 2). The resulting systems are composed of crosslinked network and linear template which interpenetrate each other to form SIPNs. The network contains both covalent and ionic bonds. The covalent bonds retain the three-dimensional structure of hydrogel and the ionic bonds bring in the hydrogel the higher mechanical strength and stimuli-sensitivity.

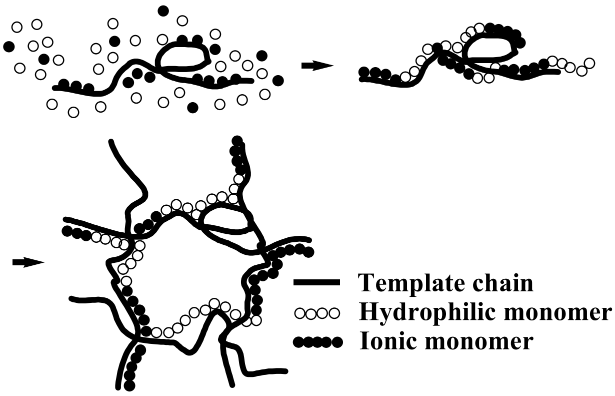

Fig. 2. Schematic representation of template (co)polymerization and formation of SIPNs structure.

The swelling behavior of SIPNs depends on network structure and nature of embedded macromolecules. Coulomb interactions or hydrogen bonds arising between the gel matrix and functional polymers have crucial effect and lead to high sensitivity and reversibility to external stimuli.

Flexible polyacrylamide (PAAm) hydrogel with embedded stiff-chain linear polyelectrolyte, sulfonated polyaniline (SPANI), has been synthesized and investigated [19]. It is shown that the incorporation of stiff-chain polyelectrolyte inside the uncharged PAAm network brings the swelling behavior different from the pure PAAm gel. Environmental pH values have remarkable influence on the swelling degree of this new gel system, the maximum swelling degree, appearing at the environmental pH value of about 12, can be 17 times greater than that at pH 1, and 12 times greater than that at pH 14. The release kinetics of SPANI has shown that SPANI is effectively retained by the gels in acidic or neutral environment, although they are not covalently attached to the network chains; but in alkaline environment, the entrapped SPANI molecules will be released into the surrounding solution gradually. The diffusion coefficient of SPANI is calculated from the experimental data. The experimental phenomena are tried to interpret from aspects of aggregation and hydrogen bonding between SPANI chains.

A series of novel SIPNs composed of poly[(acrylamide)-*co*-(sodium acrylate)] with varying amounts (5, 10, and 15 wt.%) of poly(vinylsulfonic acid sodium salt) was synthesized [20]. The swelling behavior of these SIPNs was studied in distilled water/physiological solutions/buffer solutions/salt solutions. As the amount of poly(vinylsulfonic acid sodium salt) increased in the network, the swelling capacity of the SIPNs increased considerably. The swelling and diffusion characteristics such as water penetration velocity, diffusion exponent, and diffusion coefficient were calculated in distilled water, as well as in other physiological solutions. The highest swelling capacity was noted in urea and glucose solutions. The SIPN hydrogels followed non-Fickian diffusion behavior in water and physiological fluids, whereas Fickian behavior was observed in buffer solutions. The stimuli-responsive characteristics towards physiological fluids, salt concentration, and temperature of these SIPN hydrogels were also investigated. The swelling behavior of the SIPNs decreased markedly with an increase in the concentration of the salt solutions.

The SIPNs, consisting of PNIPAAm based hydrogels and linear poly(acrylic acid) (PAAc) chains, were synthesized [21-23], and the effects of the PAAc chains on SIPNs rheology, injectability and phase behavior were analyzed. In PNIPAAm- and p(NIPAAm-*co*-AAc)-based SIPN studies, numerous reaction conditions were varied, and the effects of these factors on SIPN injectability, transparency, phase transition, lower critical solution temperature (LCST), and volume change were examined. The PAAc chains did not significantly affect the LCST or volume change of the SIPNs, compared to control hydrogels. However, the PAAc chains affected the injectability, transparency, and phase transition of the matrices, and these effects were dependent on the chain amount and molecular weight and on the interactions between PAAc chains and the solvent and/or copolymer chains in p(NIPAAm-*co*-AAc) hydrogels. These results can be used to design "tailored" PNIPAAm based SIPNs that have the potential to serve as functional scaffolds in tissue engineering applications.

Three series of SIPNs based on crosslinked PNIPAAm and 1 wt.% nonionic or ionic (cationic and anionic) linear polyacrylamide (PAAm), were synthesized to improve the mechanical properties of PNIPAAm gels [24]. The effect of the incorporation of linear polymers into responsive networks on the temperature-induced transition, swelling behavior, and mechanical properties was studied. The introduction of cationic and anionic linear hydrophilic PAAm into PNIPA networks increased the rate of swelling, whereas the presence of nonionic PAAm diminished it. SIPNs reinforced with cationic and nonionic PAAm exhibited the tensile strengths and elongations at break higher than PNIPAAm hydrogels, whereas the presence of anionic PAAm caused a reduction in the mechanical properties.

The SIPN in which the crosslinked PVA chains trap the ionic polymer were obtained by using a heat treatment at 180°C or dibromoethane vapor at 140°C, respectively, for poly(styrene sulfonic acid), poly (sodium styrene sulfonate), poly (acrylic acid) or poly (dimethyl dimethylene piperidinum chloride) as the ionic polymer [25].

A pH sensitive SIPN hydrogel based on methacrylic acid, BSA, and PEG was prepared by UV initiated free radical polymerization in the presence of light-sensitive initiator – 2,2-dimethoxy 2-phenyl acetophenone (DMPA) [26]. As a result the P(MAA-EG)-BSA SIPN was obtained as shown in Fig. 3. It was expected that due to the combined biocompatibility and biodegradability of BSA, and the pH sensitivity of the P(MAA-EG) copolymer, the obtained P(MAA-EG)-BSA SIPN may be pH-sensitive and partly-biodegradable, and may have great potential to be used in targeted drug delivery systems. The swelling behavior and pH sensitivity of these hydrogels were studied in details. With the increase in pH of the aqueous solution from 1.7 to 9.23, the swelling ratio of these hydrogels increased accordingly. The effect of BSA and crosslinker (BIS) content on the swelling behavior was more complicated. The dynamic swelling-deswelling behavior of these hydrogels was studied in the aqueous solution with alternate pH of 1.7 and 7.7. The BSA content and the crosslinker content had a significant effect on the pH sensitivity of the hydrogels.

Quaternary ammonium salt hydrogels from a cationic monomer, (3-acrylamidopropyl)-trimethylammonium chloride, in a variety sizes such as bulk, mi-

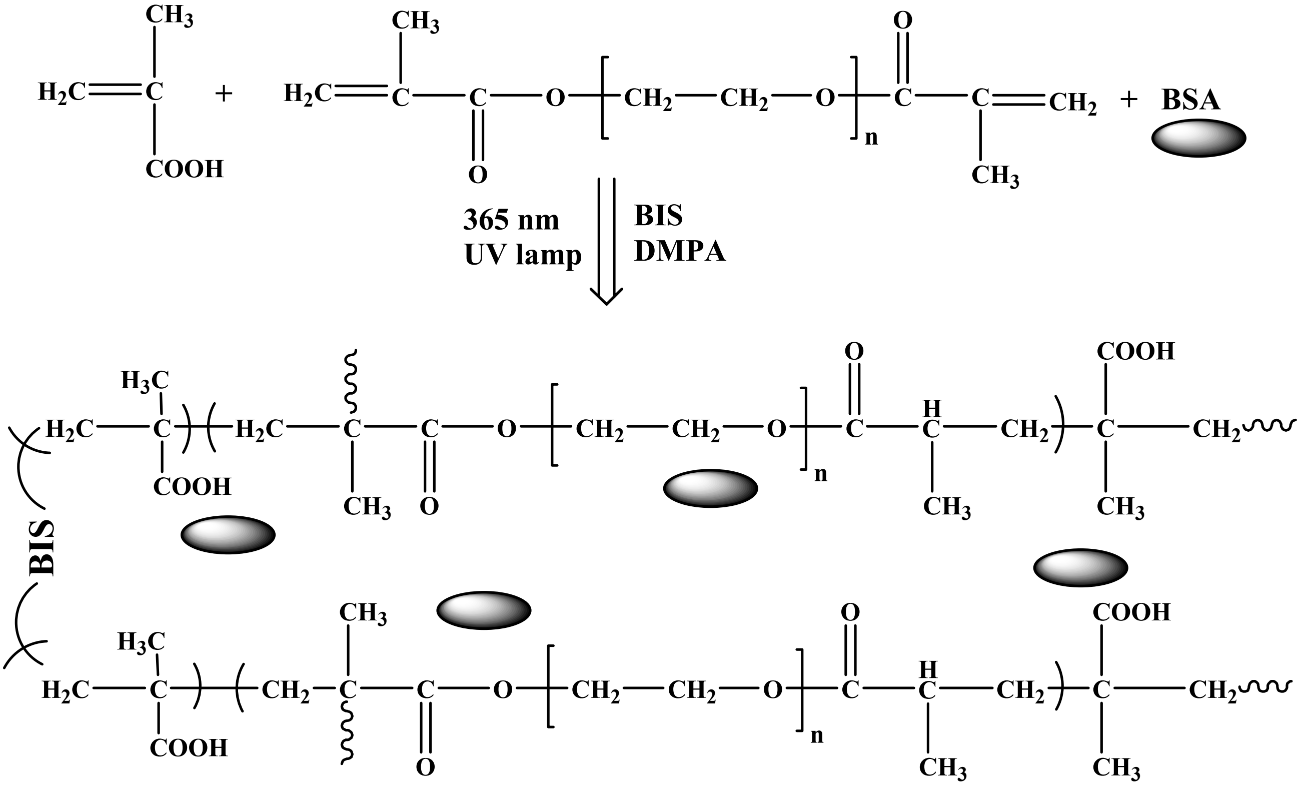

Fig. 3. Synthetic protocol of SIPN composed of P(MAA-EG) and BSA.

cro- and nano- has been prepared [27]. The synthesis of micro- and nanogels were carried out in the microenvironment of water-in-oil microemulsions using two types of surfactants, namely, *L*-α-phosphatidylcholine (lecithin) and dioctyl sulfosuccinate sodium salt. Additionally, hydrogel-hydrogel composite SIPN was synthesized by dispersing previously prepared micro/nanogel into neutral monomers such as acrylamide (AAm) or 2-hydroxylethyl methcarylate (HEMA) before network formation. Hydrogel swelling and pH response behaviors have been investigated for bulk gels. Morphology, structure, and size of nano-, micro- and bulk materials were explored utilizing transmission electron microcopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). It was confirmed by the gel electrophoresis that completely charged nanogel forms a strong complex with DNA.

The SIPNs composed of poly(dimethylaminoethylmethacrylate) (PDMAEMA) and poly(ethylene oxide) (PEO) were synthesized by γ-radiation; three SIPNs with 80:20, 90:10, and 95:5 weight ratios of DMAEMA/PEO were obtained by use of this technique [28]. The gel-dose curves showed that the hydrogels were characterized by a structure typical of SIPNs and the results of elemental analysis supported this point. The temperature-induced phase transition of SIPNs with the composition of 95:5 was still retained, with the lower critical solution temperature of PDMAEMA shifting from 40 to 27°C. The temperature sensitivity of the other two SIPNs gradually disappeared. The pH sensitivity of three SIPNs was still retained but the pH shifted slightly to lower values with increasing PEO content in the SIPNs. The effect of PEO content in semi-IPNs on their environmental responsiveness was discussed.

Preparation of amphoteric SIPNs was reported by Kokufuta and co-workers [29,30]. The behavior of amphoteric network based on terpolymer of N-isopropylacrylamide, acrylic acid and *1*-vinylimidazole was compared with SIPN based on *N*-isopropylacrylamide and *1*-vinylimidazole in volume of which linear PAAc was embedded. Both crosslinked terpolymer and SIPN exhibit amphoteric character and collapse near the isoelectric point. Nano-sized polyampholyte gel particles were synthesized by aqueous redox polymerization in the presence of sodium dodecylbenzene sulfonate as a surfactant. Acrylic acid and 1-vinylimidazole were respectively used as an anionic and a cationic monomer, both of which were incorporated into the network of *N*-isopropylacrylamide cross-linked with *N*,*N'*-methylenebisacrylamide. The intra- and inter-particle interactions were studied as a function of pH, ionic strength and temperature by static and dynamic light scattering, electrophoretic light scattering and turbidity measurements. Hydrodynamic radius of particles became minimal at the pH corresponding to an isoelectric point (pI). At pH = pI the particle swelled upon addition of salt such as NaCl, indicating antipolyelectrolyte behavior. In addition to these size changes due to intra-particle interaction, aqueous nanogel dispersions underwent a shape phase separation due to inter-particle interaction when pH and salt concentration were varied.

Amphoteric superabsorbent composite with SIPN composed of PAA/Ca-bentonite/PDMDAAC was prepared by a combination of intercalative polymerization and a sequential IPN method and the effects of reaction parameters on the swelling capacity were studied [31]. PDMDAAC was used as a polycation to modify bentonite and form SIPN with lightly crosslinked PAA. FTIR and TG were used to characterize the amphoteric superabsorbent composites with SIPN. The thermal stability of the product was not degraded as in the case of using small molecular surfactant to modify bentonite. The contents of carboxylic groups and nitrogen had been determined. This indicated that the product with certain content of carboxylic groups and nitrogen is inclined to exhibit excellent swelling capacity. The presence of PDMDAAC improved the swelling capacity. The resulting amphoteric superabsorbent composite showed excellent swelling capacity of 1578 g/g in distilled water and 136 g/g in 0.9 wt.% NaCl solution.

The SIPNs can also be obtained by interpolymer reactions, *e.g.* by interaction of ionic or nonionic polymer gels with linear macromolecules at the gel-solution interface [32-34]. The specific peculiarity of interpolymer reactions reviewed in [35] is the cooperative character of interaction proceeding via "relay-race" mechanism resulting in gel contraction (Fig. 4).

Sorption mechanism of linear polyelectrolytes by crosslinked polyelectrolyte hydrogels includes two independent interpolyelectrolyte reactions. The adsorption rate is represented by "relay race" transfer of polyion segments from one fragment of the network to another (vacant). Each transfer act taking place at the shell/core interface and directed towards hydrogel phase leads to formation of vacancy in shell part of crosslinked polyelectrolyte which in turn is accessible to another polyion segment for transfer in

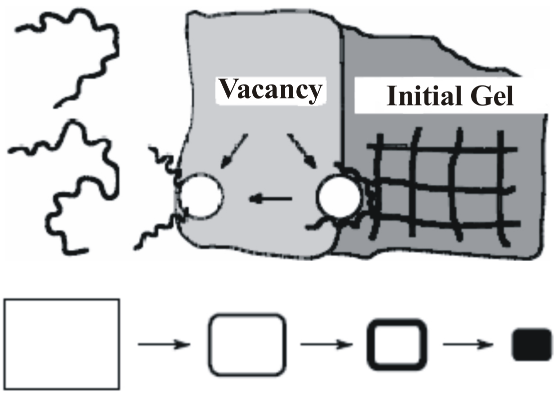

Fig. 4. Sorption mechanism of linear polyelectrolytes by crosslinked polyelectrolyte hydrogel.

the same direction. As a result the shell/core interface moves to the center of hydrogel specimen. At the same time the charged vacancies together with neutralizing them counterions move to opposite direction and finally reach the interface between the shell of crosslinked polyelectrolyte and external solution. Here they are bound with inflowing from the solution oppositely charged linear polyions. Such reaction creates the driving force that is necessary for migration of polyions into oppositely charged hydrogel. In other words, free energy of complexation reaction goes to polyions transport in hydrogel phase "pushing" the reaction. If the interpolyelectrolyte complexation reaction does not occur, then linear polyions do not penetrate inside of crosslinked polyelectrolyte. In such case only thin adsorbed films are formed on the surface of hydrogels. Table 1 demonstrates some examples of interpolyelectrolyte reactions proceeding on gel-solution interface.

Semi-interpenetrating hydrogels of polyelectrolytes consisting of poly(acrylamide) hydrogel (PAAm) and sodium poly(styrenesulfonate) (PSSNa), poly(*N,N′*-dimethyl-*N,N′*-diallylammonium chloride) (PDMDAAC) and stoichiometric interpolyelectrolyte complex of PSSNa-PDMDAAC were prepared by template polymerization: crosslinked acrylamide chains were formed in aqueous solutions of PSSNa, PDMDAAC, and PSSNa-PDMDAAC respectively in the presence of *N,N′*-methylenebisacrylamide [36-39]. The swelling degrees of SIPNs determined in water were equal to 12±1 g/g. It was found that the dynamic swelling behavior of SIPNs in aqueous solution corresponds to relaxation-controlled mechanism. The influence of 0.1 N HCl, 0.1 N NaOH, pH, ionic strength, water-acetone (ethanol) solvent mixture on swelling-deswelling behavior of SIPNs was studied. The SIPNs composed of PAAH/PSSNa-PDMDAAC were also obtained by interpolymer reactions at gel-solution interface, *e.g.* by interaction

**Table 1**

Complexation of crosslinked polyelectrolyte hydrogels with oppositely charged linear polyelectrolytes at 293 K

| Linear polyelectrolyte | $M_w$ | Crosslinked polyelectrolyte | Complexation peculiarity |
|---|---|---|---|
| Poly-4-vinylpyridine | $3\cdot10^{-5}$ | Sodium polyacrylate | Penetration |
| | $1.5\cdot10^{-5}$ | | Penetration |
| | $0.5\cdot10^{-5}$ | | Penetration |
| Poly-*N*,*N*-dimethylamino-ethylmethacrylate | $6\cdot10^{-4}$ | | Penetration |
| Polyethyleneimine | $6\cdot10^{-4}$ | | Penetration |
| Chitosan | $2\cdot10^{-5}$ | | Penetration |
| Copolymer of *N*-ethyl-4-vinylpyridinium and *N*-dodecyl-4-vinylpyridinium (70:30 mol.%) | $1.7\cdot10^{-3}$ | | Adsorption |
| Sodium polyacrylate | $3.5\cdot10^{-5}$ | Poly-*N*,*N*-dimethylamino-ethylmethacrylate | Penetration |
| Sodium polymethacrylate | $2.7\cdot10^{-4}$ | | Penetration |
| | $1.6\cdot10^{-4}$ | | Penetration |
| Sodium polystyrenesulfonate | $3\cdot10^{-5}$ | | Adsorption |
| Sodium polyvinylsulfate | $4.4\cdot10^{-4}$ | | Adsorption |
| Heparin | $1\cdot10^{-5}$ | | Adsorption |

of PAAm/PSSNa gel with linear PDMDAAC or PAAm/PDMDAAC gel with linear PSSNa (Fig. 5). The interpolyelectrolyte reactions between the gel matrix and linear polyelectrolytes proceed *via* "relay-race" mechanism resulting in gel contraction [32]. Stoichiometric interpolyelectrolyte complex PSSNa-PDMDAAC immobilized into the neutral polyacrylamide hydrogel shows amphoteric character and has a minimum swelling at pI = 6.8.

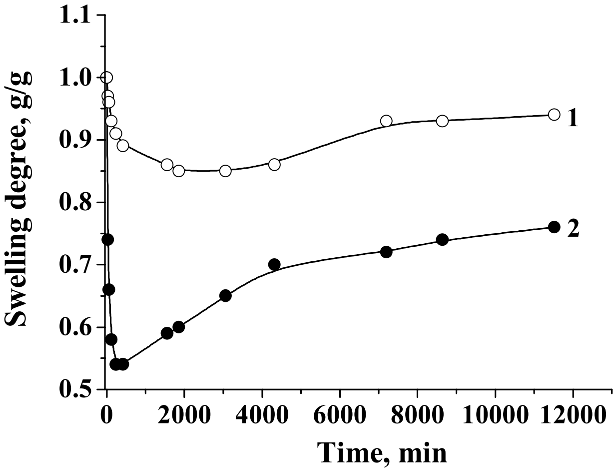

Fig. 5. Diffusion of PSSNa into the SIPN of PAAm/PDMDAAC (1) and diffusion of PDMDAAC into the SIPN of PAAm/PSSNa (2).

Complexes of polyvinylpyrrolidone-polyacrylic acid (PVP-PAA) photopolymerized from a mixture of PVP and acrylic acid (AA) were characterized by means of DSC and FTIR spectrometry [40]. The swelling of PVP-PAA SIPN films was studied in various pH media. The results showed that swelling in 0.1 N HCI solution and pH 3.0 phosphate buffer was strikingly different from that in the pH 6.0 phosphate buffer. Caffeine release rate from the SIPN film followed Fick's Law. Control of caffeine release from the SIPN film was realized by changing cyclically the pH of dissolution medium between 0.1 N HCI solution and pH 6.0 phosphate buffer.

It is found that acrylamide gel shows combined collapse-swelling behavior in dilute aqueous solution of poly(vinyl methyl ether) when transferred from the equilibrium swelling state in pure water [41]. Namely, it starts to collapse quickly and then it is swollen again with its volume approaching the original value in water. The phenomenon can be explained by thermodynamic analysis of osmotic pressure. The re-swelling is caused by the penetration of linear polymer into the network. The analysis can also explain differences in the collapsing and re-swelling behavior between the samples with different shapes.

The organic-inorganic hybrid thermosensitive SIPN hydrogels have been synthesized based on the sol-gel technology [42]. These "intelligent" hybrid materials consisting of inorganic silica phase and an organic polymer phase show a LCST in aqueous solution. As organic phase thermosensitive polymers that exhibit different phase separation mechanisms, have been chosen: poly(*N*-vinylcaprolactam) (PVCL), poly(*N*-isopropylacrylamide) (PNIPAA) and poly(methyl vinylether) (PMVE). The inorganic phase consists of silica particles synthesized by the sol-gel process. FTIR spectroscopy proved the existence of hydrogen bonding between linear polymer molecules and silica particles. These hydrogen bonds are caused by the silanol groups of the silica particles and the carbonyl or ether function of the polymer. PVCL hybrid gels show continuous deswelling, PNIPAA hybrid gels show discontinuous deswelling, PMVE hybrid gels show normally discontinuous deswelling, but the influence of silica is dominant and changes the shrinking behavior completely. Cloud point temperatures decrease if the silica fraction in the hybrid material increases. This is due to the competition between the silanol groups and water to interact with the polymer. The swelling rate is many times lower than the deswelling rate. The swelling process is determined by the water diffusion, whereas in the deswelling the hydrophobic interactions between the polymers play a major role. Silica improves the mechanical stability but lowers the elasticity of the hybrid hydrogels.

## Alginate- and Chitosan-based SIPNs

Weakly ionizable polysaccharides, such as alginate and chitosan, show pH responsive phase transition. Alginate is an acidic polysaccharide bearing carboxylic groups, whose $pK_a$ is at 3-4 (Fig. 6a). The use of alginate as the starting material is advantageous because it is available from more than one source, and is available in good purity and characterization. Chitosan exhibits basic rather than acidic characteristics that are usually shown in other polysaccharides. Chitosan is the *N*-deacetylated derivative of chitin and is shown as a copolymer consisting of 2-acetamido-2-deoxy-*b*-*D*-glucopyranose and 2-amido-2-deoxy-*b*-*D*-glucopyranose (Fig. 6b).

The amine groups in chitosan gain protons at low pH and release them at high pH. Therefore, this

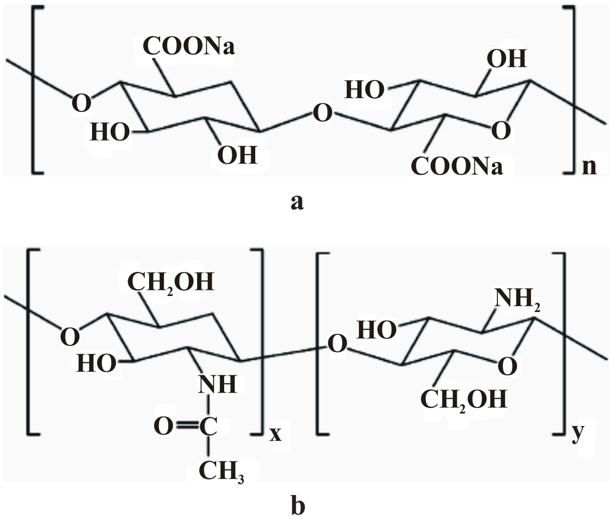

Fig. 6. Repeating units of sodium alginate (a) and chitosan (b).

biopolymer shows precipitation over pH 6-6.2 due to high hydrogen bonding strength between –OH groups and uncharged amine groups in chitosan chains. These compact crystalline structures are broken and resolubilized under weakly acidic conditions. Further, chitosan is a nontoxic natural polysaccharide and is compatible with a living tissue. These appealing features make chitosan widely applicable in wound healing, production of artificial skin, food preservation, cosmetics, and wastewater treatment *etc*. Synthesis and characterization of hydrophobically modified polysaccharides including alginate and chitosan have been reviewed in [43].

The pH-responsive SIPN hydrogels based on linear sodium alginate (SA) and cross-linked PNIPAAm were prepared [44]. Compared with the conventional PNIPAAm hydrogel, the deswelling rate of SIPN in response to temperature was improved significantly, owing to the formation of a porous structure within the hydrogels in the presence of ionized SA during the polymerization process. Moreover, the deswelling process could be well described with a first-order kinetics equation and it is possible to design any hydrogel with the desired deswelling behavior through the control of the SA content in the SIPN hydrogels.

SIPN hydrogels, composed of alginate and amine-terminated PNIPAAm, were prepared by crosslinking with calcium chloride [45]. From the swelling behaviors of SIPNs at various pH's and FTIR spectra at high temperatures, the formation of a polyelectrolyte complex was confirmed from the reaction between carboxyl groups in alginate and amino groups in modified PNIPAAm. The water state in hydrogels, investigated by differential scanning calorimetry, showed that [alginate/PNIPAAm (w/w) = 50/50] exhibited the lowest equilibrium water content and free water content among the hydrogels tested, which was attributed to its more compact structure compared to other samples and the high content of interchain bonding within the hydrogels. Alginate/PNIPAAm SIPN hydrogels exhibited a reasonable sensitivity to the temperature, pH, and ionic strength of swelling medium.

The SIPN and IPN composed of alginate and PNIPAAm were prepared with γ-ray irradiation [46]. The SIPN hydrogels were prepared through the irradiation of a mixed solution composed of alginate and NIPAAm monomer to simultaneously achieve the polymerization and self-crosslinking of NIPAAm. The IPN hydrogels were formed through the immersion of the semi-IPN film in a calcium-ion solution. The results for the swelling and deswelling behaviors showed that the swelling ratio of SIPN hydrogels was higher than that of full-IPN hydrogels. A SIPN hydrogel containing more alginate exhibited relatively rapid swelling and deswelling rates, whereas a full-IPN hydrogel showed an adverse tendency. All the hydrogels with NIPAAm exhibited a change in the swelling ratio around 30-40°C, and full-IPN hydrogels showed more sensitive and reversible behavior than SIPN hydrogels under a stepwise stimulus. In addition, the swelling ratio of the hydrogels continuously increased with the pH values, and the swelling processes were proven to be repeatable with pH changes.

Temperature-, pH- and electro-responsive SIPN hydrogels were constructed from chitosan (CS) and poly(diallyldimethylammonium chloride) (PDADMAC) [47,48]. CS/PDADMAC SIPN hydrogels exhibited a relatively high swelling ratio and DSC was used for the quantitative determination of the amounts of freezing and nonfreezing water. The amount of free water increased with increasing PDADMAC content in the SIPN hydrogels. The swelling behavior of the CS/PDADMAC SIPN hydrogels was studied through the immersion of the gels in various concentrations of aqueous NaCl solutions, and their responses to stimuli in electric fields were also investigated. When the swollen SIPN hydrogels were placed between a pair of electrodes, they exhibited bending behavior upon the application of an electric field, which was stepwise and dependent on the magnitude of the field.

Chitosan/poly(ethylene glycol) [49], chitosan/poly(hydroxy ethyl methacrylate) [50,51] and chitosan/poly(vinyl pyrrolidone) [52] SIPNs were prepared and characterized. The effects of pH, temperature, and an electric-field on the swollen SIPNs were investigated. The swelling kinetics of chitosan and poly(hydroxy ethyl methacrylate) hydrogels increased rapidly, reaching equilibrium within 60 min. SIPN hydrogels exhibited relatively high swelling ratios, 150-350%. The swelling ratio increased when the pH of the buffer was below pH 7 as a result of the dissociation of ionic bonds. The swelling behavior of the chitosan/poly(hydroxy ethyl methacrylate) hydrogels was studied by immersing the gels in various concentrations of aqueous NaCl solution. SIPN hydrogels showed electro-responsiveness by shrinking when an electric field was applied. When the SIPN hydrogels were swollen, where one electrode was placed in contact with the gel and the other fixed 30 mm apart from one, they exhibited bending behavior on the application of an electric field on a contact system. The electro-responsive behavior of the present semi-IPN was also affected by the electrolyte concentration in the external solution. The SIPN also showed various degrees of increased bending behavior depending on the electric stimulus. A viscous solution of chitosan and poly(ethylene glycol) in 2% acetic acid was extruded as droplets with the help of a syringe and crosslinked using glutaraldehyde. The structural studies of the beads were performed by using a Fourier transform infrared spectrophotometer and scanning electron microscope. The swelling behavior, solubility, hydrolytic degradation, and loading capacity of the beads for isoniazid were investigated. The structural changes of the beads at pH 2.0 and 7.4 were put forward using the data obtained by infrared and ultraviolet spectroscopy. The prepared beads showed 82% drug-loading capacity, which suggested that these semi-interpenetrating polymer network beads are suitable for controlled release of drugs in an oral sustained delivery system. The chitosan/poly(vinyl pyrrolidone) hydrogels were crosslinked using genipin, a non-toxic cross-linking agent extracted from the fruits of *Gardenia jasminoides Ellis*. Swelling properties of these hydrogels were studied in a media with different pH and temperatures. The states of water in the swollen hydrogels at 25°C and pH 7 were determined using DSC. The swelling behavior of the hydrogels was found to be dependent on the temperature and the pH of the swelling medium. The total water content in the hydrogels was found to increase with increasing PVP content.

SIPN and IPN gels with thermo-sensitivity were prepared by introducing a biodegradable polymer, chitosan, into the PNIPAAm gel system [53]. The swelling behavior, morphology, temperature sensitivity, pH sensitivity, gel strength, and drug-release behavior of PNIPAAm/chitosan SIPN and IPN hydrogels were investigated. The results indicated that the PNIPAAm/chitosan SIPN and IPN hydrogels exhibited pH and temperature-sensitivity behavior and could slow drug release and diffusion from the gels. From the stress-strain curves of the hydrogels, the compression moduli of IPN gels containing crosslinked chitosan were higher than those of SIPN gels. This is because IPN gels have a more compact structure.

The synthesis and characterisation of semi-interpenetrating polymeric networks obtained by the radical-induced polymerization of *N*-isopropylacrylamide in the presence of chitosan using tetraethyleneglycoldiacrylate as the crosslinker is described [54]. The influence of the degree of crosslinking and that of the ratio of chitosan to PNIPAAm on the "pH/temperature induced" phase transition behavior and swelling characteristics of the hydrogel system are investigated. The ability of the same system to act as a controlled release vehicle for pilocarpine hydrochloride is evaluated.

*In vitro* studies have been carried on SIPN beads of chitosan-alanine as a carrier for the controlled release of chlorpheniramine maleate (CPM) drug [55]. The swelling behavior of crosslinked beads in different pH solutions was measured at different time intervals. The structural and morphological studies of beads were carried out by using a SEM. The drug release experiments of different drug loading capacity beads performed in solutions of pH 2 and pH 7.4 using CPM as a model drug showed that chitosan-alanine crosslinked beads are suitable for controlled release of drug.

## Gel-immobilized Catalysts and Nanoparticles

Natural enzymes catalyze chemical reactions and regulate such reactions by reversibly and repeatedly switching their catalytic activities "on and off" [56]. The authors [57] reported the development of a polymer gel with a catalytic activity that can be switched "on and off" when the solvent composition is changed. The gel consists of two species of monomers. The major component, *N*-isopropylacrylamide, makes the gel swell and shrink in response to a change in composition of ethanol/water mixtures. The minor component, vinylimidazole, which is capable of catalysis, is copolymerized into the gel network to give SIPN. The reaction rate for catalytic hydrolysis of *p*-nitrophenyl caprylate was small when the gel was swollen. In contrast, when the gel was shrunken, the reaction rate increased 5 times. The activity changes discontinuously as a function of solvent composition, thus the catalysis can be switched "on and off" by an infinitesimal change in solvent composition. The kinetics of catalysis by the gel in the shrunken state is well described by the Michaelis-Menten formula, indicating that the absorption of the substrate by the hydrophobic environment created by the *N*-isopropylacrylamide polymer in the shrunken gel is responsible for enhancement of catalytic activity. In the swollen state, the rate *vs*. active site concentration is linear, indicating that the substrate absorption is not a primary factor determining the kinetics. Catalytic activity of the gel is studied for substrates with various alkyl chain lengths; of those studied the switching effect is most pronounced for *p*-nitrophenyl caprylate.

The metal-ion complexation behavior and catalytic activity of crosslinked poly(acrylic acid) were investigated [58]. The metal uptake followed the order: Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Zn(II) > Ni(II), while the catalytic activity toward the hydrolysis of *p*-nitrophenyl acetate decreased in the order Co(II) > Ni(II) > Cu(II) > Zn(II) > Cr(III) > Mn(II) > Fe(III). The effect of various parameters such as time, temperature, amount of catalyst, pH, and concentration of buffer had vital role in the hydrolysis of *p*-nitrophenyl acetate.

Catalytic properties of SIPNs composed of acrylamide gel matrix and copper (II) complexes of poly(ethyleneimine) were studied with respect to hydrogen peroxide decomposition [59]. The freshly prepared SIPN catalyst exhibited lower catalytic activity but its activity considerably increased after one day (Fig. 7). This is probably explained by the accessibility of catalytic centers of SIPN due to the network swelling. The mechanism of hydrogen peroxide decomposition in the presence of homogeneous and heterogeneous catalysts is discussed.

SIPNs of poly(ethylene glycol), poly(vinyl alcohol) and polyacrylamide were prepared as a support for enzyme immobilization and kinetic studies were performed for the immobilization of α-amylase [60]. The effect of SIPN composition on the extent of immobilization was investigated and the percentage of relative activity of the immobilized enzyme was evaluated as a function of the chemical architecture of the SIPNs, pH and temperature, taking starch as a substrate. The kinetic constants and the maximum reaction velocity were also evaluated. The SIPNs were characterized by IR spectral analysis.

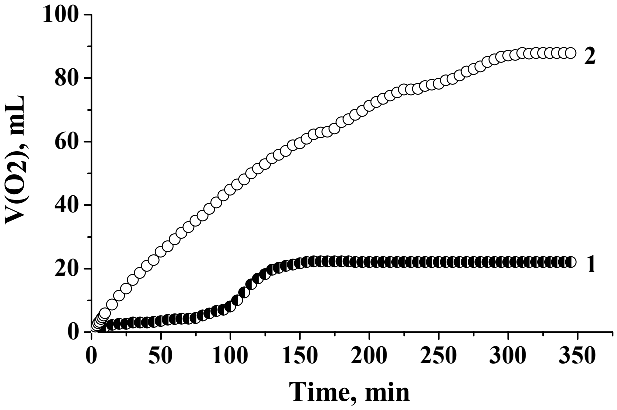

Fig. 7. Decomposition of $H_2O_2$ in the presence of freshly prepared SIPN catalyst (1) and the same catalyst after one day (2).

In recent years, various composite materials consisting of colloidal nanoparticles, such as Pd, Au or Ag, embedded in AAm and PNIPAm hydrogels were synthesized and used as novel catalysts [61,62], antibacterial materials [63] and drug delivery vehicles [64]. For instance, a novel method, forming Au nanoparticles inside an existing PNIPAm template, was recently developed [61]. A hydrogel is first synthesized by crosslinking polymerization of NIPAm and crosslinkers containing thiol groups that bind both $Au^{3+}$ ions and stabilize the colloidal Au. The functionalized hydrogel matrix then modulates the formation of colloidal Au nanoparticles after the addition of a reductant, such as $NaBH_4$. Compared with the non-Au containing PNIPAm hydrogels, the Au-PNIPAm nano-composite hydrogels have shown higher degrees of equilibrium swelling and different temperature-triggered phase transitions.

Hydrogels offer large free space between the crosslinked networks in the swollen stage that can act as a nanoreactor for the nucleation and growth of the nanoparticles. Protected by poly-*N*-vinylpyrrolidone (PVP) palladium and silver nanoparticles with the average diameters 20-60 nm were embedded in polyacrylamide hydrogel matrix [65]. Hydrogel-immobilized metal nanoparticles were obtained by template polymerization: crosslinked acrylamide chains were formed in water-methanol or ethanol solutions containing colloidal dispersions protected by PVP (Fig. 8). Protective action of PVP prevents the coagulation of small metal particles. Metal nanoparticles are uniformly dispersed and highly stabilized throughout the macromolecular chain, forming uniform metal-polymer composite materials (Fig. 9).

The influence of pH, ionic strength, water-acetone (ethanol) solvent mixture on the swelling-deswelling behavior of the hydrogel-coated Pd and Ag nanoparticles was studied. Information on structure and morphology of hydrogel-coated nanometals was provided by SEM and TEM. Nanometals supported on SIPN exhibited high catalytic activity in hydrogenation of various unsaturated organic compounds. It was shown that the reaction rate is limited by diffusion of the substrates into the swollen polymer phase.

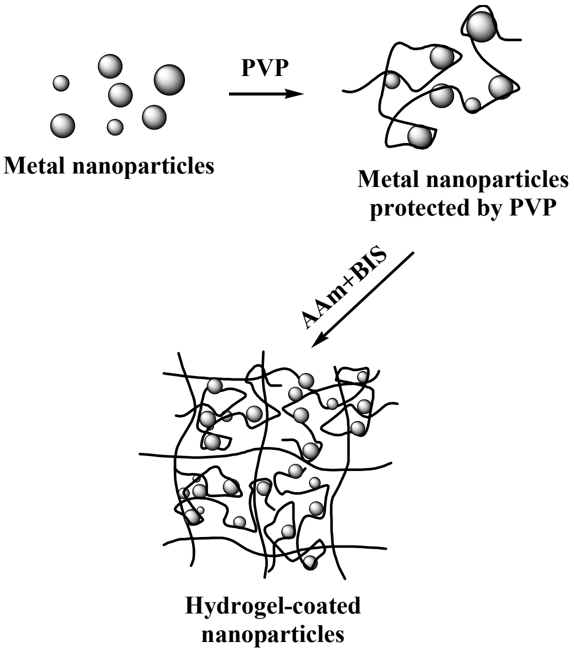

Fig. 8. The SIPN formation process using metal nanoparticles protected by linear polymers.

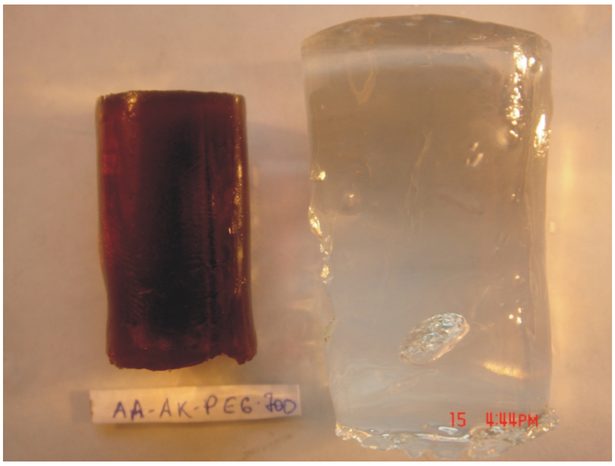

Fig. 9. Photographs of SIPN containing the Pd nanoparticles (left) and initial SIPN (right).

## Application Aspects of SIPNs

Application aspects of SIPNs cover drug delivery systems [49,54,55], matrixes for enzyme immobilization [66], ion-exchange membranes [25,67], catalysts [68] *etc*. Compositions for tissue engineering and drug delivery have been developed based on solutions of two or more polymers which form SIPNs upon exposure to active species following injection at a site in a patient in need thereof [69].

The adsorption of fibrinogen (Fgn) onto the surface of SIPNs of poly(ethylene glycol) (PEG) and poly(2-hydroxyethyl methacrylate) (PHEMA) was provided by the authors [66]. The SIPNs were prepared by polymerizing 2-hydroxyethyl methacrylate with a redox system and in the presence of PEG and crosslinker ethyleneglycol dimethacrylate. The proposed spongy SIPNs were characterized by FTIR and SEM. The network structural parameters, such as molecular weight between crosslinks and crosslink density, were calculated using swelling measurements. The adsorption of Fgn was carried out onto the spongy SIPNs and kinetic constants of the adsorption process as well as isotherm constants were evaluated. The adsorption process was also studied under varying pH, ionic strengths, and chemical architecture of the SIPNs. The anti-thrombogenic behavior of the polymer matrices was judged using *in vitro* tests.

SIPN membranes were prepared by blending poly(vinyl alcohol) (PVA) with different ionic polymers [49,67]. SIPNs in which the crosslinked PVA chains trap the ionic polymers were obtained by using a heat treatment at 180°C or dibromoethane vapor at 140°C, respectively, for poly(styrene sulfonic acid) (PSSH), poly(sodium styrene sulfonate) (PSSNa), poly(acrylic acid) (PAAc) polyethyleneimine, and poly(dimethyl dimethylene piperidinium chloride) as the ionic polymer. Membranes with PVA (60%) and polyelectrolytes (40%) showed the best compromise among mechanical, homogeneous, and ion-exchange properties. The best results (large ion-exchange capacity and small swelling ratio) were obtained for PVA/PAAc and PVA/PSSNa/PSSH membranes. Among anion-exchange membranes, PVA/PEI gave the best permselectivity (low co-ion leakage) and the highest ion-exchange capacity. The stability of the SIPN membranes in some liquid media was studied to select the appropriate membranes for the envisaged applications. The thermally crosslinked PVA/PSSH membranes showed an effective catalytic effect on the esterification reaction between *n*-propanol and propanoic acid. An active composite membrane made of a layer of PVA/PSSH deposited on a dense PVA layer of an industrial dehydration membrane exhibited both high catalytic activity and high selectivity to water in the pervaporation-assisted esterification. The values of the counter-ion transport number indicated that some crosslinked ionic membranes have good ion permselectivity.

The SIPN and IPN membranes were prepared [70] from a mixture system of poly(4-vinylpyridine) (P4VP) and poly(glycidyl methacrylate) (PGMA) by quaternizing crosslinking of P4VP with 1,4-dibromobutane (DBB) and by simultaneous crosslinking of P4VP with DBB and PGMA with tetraethylenepentamine (TEPA), respectively. The difference between SIPN and IPN was demonstrated by IR, tensile strength, and dimension stability. The membrane performance in pervaporation for ethanol-water mixtures and reverse osmosis was investigated. The polymer mixture of 1:1 on a monomer base with 30 mol.% DBB on the 4VP unit and 5.6-7.5 mol.% (8-10 wt.%) TEPA on the GMA unit gave an optimum membrane performance. Those crosslinked membranes were stronger than was the cellulose acetate membrane, mostly owing to the PGMA chains, and exhibited a high separation factor for the azeotropic feed in pervaporation. IPN membranes generally showed a performance higher than that of the SIPN ones. An attempt to improve the product rate was made by the addition of a water-soluble polymer to the membrane on casting. The separation factor for solubility in the membrane at the feed side dominated the overall separation factor, particularly for feeds of higher ethanol concentrations.

SIPN membranes based on novel sulfonated polyimide (SPI) and poly (ethylene glycol) diacrylate (PEGDA) have been prepared for the fuel cell applications [71]. SPI was synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride, 4,4'-diaminobiphenyl 2,2'-disulfonic acid, and 2-bis[4-(4-aminophenoxy) phenyl]hexafluoropropane. PEGDA was polymerized in the presence of SPI to synthesize SIPN membranes of different ionic contents. These membranes were characterized by determining, ion exchange capacity, water uptake, water stability, proton conductivity, and thermal stability. The proton conductivity of the membranes increased with increasing PEGDA content in the order of $10^{-1}$ S·cm$^{-1}$ at 90°C. These SIPN membranes showed higher water stability than the pure acid polyimide membrane. This study shows that SIPN membranes based on PEGDA which gives hydrophilic group and structural stability can be available candidates comparable to Nafion® 117 over 70°C. The perspective application of semi-interpenetrating polymer networks with temperature-dependent light transmission for solar technology was demonstrated by authors [72]. It was shown [73] that SIPNs due to high elasticity, good mechanical durability and stimuli-sensitivity can be used as hydrogel "cleaners" for cleaning the internal surface of main pipes.

## Conclusions

Thus the literature survey shows that the SIPNs are perspective "smart" composite materials fast developing during the last 10 years. The synthetic strategy of SIPNs preparation includes template polymerization (fast) in solution or bulk and interpolymer reactions (slow) on gel-solution interface. Both synthetic and natural polymers including inorganic polymers, micro- and nanogels, nanoparticles may be embedded into the hydrogel network resulting in improvement of the mechanical properties, biocompatibility, to be as carrier for the controlled release of drugs, and to design stimuli-sensitive compositions. Structure, morphology, physico-chemical and physico-mechanical properties of SIPNs are determined by both network structure and immobilized linear polymers. The SIPNs can be applied in medicine, biotechnology, catalysis, environmental protection and oil industry.

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